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No charge is made for ENDEAVOUR. It is distributed to senior scientists, scientific institutions, and libraries throughout the world, the guiding principle being that of helping scientists overseas to maintain those contacts which their British colleagues have always so much valued. Within these limits the Editors are at all times glad to consider the addition of new names to the mailing list.

The drawing on the cover is of the bark Endeavour, *which, commanded by Captain James Cook and carrying a number of scientific workers, was sent out by the British Admiralty in* 1768 *to chart the South Pacific Ocean and observe the transit of Venus*

ENDEAVOUR

A quarterly review designed to record the progress of the sciences in the service of mankind

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The language of science

The progress of science depends upon many factors, and not least among these is the existence of satisfactory arrangements for the rapid exchange of new ideas and experimental results between research workers having similar interests. In a branch of learning that prides itself particularly upon its powers of systematization it is surprising that in this respect so much has been left to chance and so little has been done to formulate and follow an agreed policy appropriate to modern needs. There is, of course, no lack of scientific literature, both books and journals: the 'World List of Scientific Periodicals' now lists some 50 000 titles. Indeed, almost every scientist now finds it impossible to read all the work relevant to his own subject, far less to read extensively outside it. Yet wide reading is becoming increasingly important, for it is very frequently in the fields where several branches of science overlap that the most exciting results are obtained.

While this problem of the sheer quantity of literature is a serious one, it is at least one to which some effective answers have been found and applied. Most important, of course, are the various abstracting services, the value of whose work needs no emphasis here. Moreover, the large number of scientific periodicals is not wholly a bad thing: the less important ones serve to some extent as a filter, though by no means a completely efficient one, that reserves work of proved importance for journals of wider circulation and higher standing.

The no less important question of the language in which scientific work should be presented remains, however, largely unresolved. It is, like so many others in the modern world, one on which it is generally agreed that an international policy is urgently necessary but on which it is in fact difficult to get any agreement at all. Clearly, the problem is one which no amount of good will and harmonious agreement can solve quickly; this is an additional reason for deciding upon the ultimate goal and trying to agree upon a policy by which it may be achieved. In the meantime the barrier of language keeps many scientists in prolonged ignorance of work of immediate importance to them being done in many countries. With the rapid expansion of scientific research in countries whose contribution has hitherto been relatively small the problem is rapidly becoming more serious.

The general facts of the situation are easily ascertained and occasion no controversy. It is established, for example, that much of the world's scientific literature is published in a language unintelligible to more than half the world's scientists. The distribution of journals according to language shows a wide variety. Roughly speaking, some 44 per cent of scientific journals are published in English, 14 per cent in German, 13 per cent in French, 8 per cent in Russian, 5 per cent in Spanish, 4 per cent in Italian, and the remainder in the other languages of the world. Such figures cannot be exact, and they vary from one branch of science and technology to another, but they certainly indicate the general situation. Moreover, these proportions can be expected to change fairly rapidly. Unless some major change of policy occurs, the proportion of papers appearing in the Russian language is bound to rise rapidly. There is every reason to expect that the scientific literature of China will grow rapidly, and it is likely that, if only for political reasons, much of this will be published in Chinese, with Russian the second choice. It is possible that Hindi and other languages at present unfamiliar to the Western world may in time become important scientific languages. In the absence of positive action the situation is bound to become steadily more complicated and difficult to resolve.

Supposing—and in present circumstances it is a supposition requiring a good deal of optimism—that international agreement could be obtained to mitigate these difficulties, what is the proper policy to pursue? Three principal courses are clearly open to us, presuming that the present one of laissez-faire is rejected. Firstly, we might aim at the ideal of a single language for the communication of all scientific work. Secondly, a limited number of languages, selected from those already most widely used for scientific purposes, might be selected. Thirdly, more extensive use could be made of professionally prepared translations.

In considering these general proposals it is necessary to consider both short-term and long-term policy. To satisfy immediate needs, taking the situation as it is and not as one might wish it to be, the extension of translations between languages is the only possible policy. This has, of course, been recognized by ENDEAVOUR since its inception in 1942: at the present time we look upon our foreign-language editions as indispensable to our object of providing an internationally

useful review of the progress of science. The recent great expansion of professional interlingual scientific translation is evidence that this view is generally accepted. Much of this expansion has, of course, been occasioned by the relatively sudden efflorescence of science in Russian, which has introduced a novel factor into the situation. Here we have a sudden and unprecedented flow of important scientific work in a language with which the scientific world in general is not merely unfamiliar but totally ignorant. In the circumstances no choice is open to the West: for the moment the work must be followed through translations or not at all. It should be remarked that this situation apparently does not exist in reverse. At least fifty per cent of Russian scientists and technologists are reputed to be able to read English, French, or German, and many are said to know more than one of these languages.

Indispensable though it is, there are obvious reasons against indefinite extensions of the translation system. It is wasteful of time, money, and scientific manpower; it causes delay; and it can lead to misunderstanding. So far as the last point is concerned, it is perhaps not generally realized how difficult it is to make really accurate translations of highly technical material. In fields developing rapidly, essential words may not even have been coined in certain languages, and only knowledgeable circumlocution can render the sense accurately. While an increase in translation services seems inevitable over the next few years, it is a process not without danger. It will lead to the evolution of an extensive and expensive organization whose very existence will be prejudicial to the adoption of alternative policies that may in the long run be more satisfactory.

A universal language for all scientific communication is obviously desirable on many grounds, but both its choice and its achievement are likely to be beset by great difficulties. The choice of any single language for the communication of results in so important a field would naturally be beset by all kinds of political and nationalistic obstacles. Many of these might be overcome if one adopted a non-living language such as Latin or an artificial language such as Esperanto or Interlingua. Artificial languages are open to the fundamental objection that their very nature and purpose make them unsuitable for conveying subtle shades of meaning: they are satisfactory enough for describing facts but inadequate for conveying ideas, especially unfamiliar ones. Latin is free from this defect, for in its long evolution it acquired considerable flexibility. Its evolution virtually stopped, however, before modern science began. Its present vocabulary and syntax are therefore inappropriate for modern needs, as is well known to every university orator who has been called upon to describe in Latin the work of scientists. It is a great pity that Latin was allowed to lapse as the international language of scholars, but it is doubtful whether it is now feasible to revive it.

The choice of a single language would have the great and obvious advantage that nobody would be required to learn more than one language other than his own. The argument in its favour is further strengthened by the consideration that for the innovation to be effective it would be necessary for all scientists to be able not merely to read this language—a facility that could be acquired without great difficulty—but to write in it, which is very much more difficult. To learn to write well in even one foreign language is for the ordinary person a considerable and time-consuming achievement.

A compromise, by which two or three modern languages only are accepted for universal use in science, seems more likely to achieve success, but even if a decision were taken today it could have effect only after many years. For this to be effective, it would be necessary to institute educational reforms in many countries, for real proficiency in a foreign language is not easily acquired without formal study. These, even if achieved, could not bear fruit for a long time. The certainty of difficulty is, however, no argument for making no attempt to reach a generally acceptable policy. At least the teaching of languages is a feature of most national curricula, and it ought not ultimately to be impossible, when so much is at stake, to agree upon the substitution of one for another when necessary.

The barrier of language is harmful in science, but it is, of course, an equally serious obstacle in all fields of learning, in politics, in industry and commerce, and in every kind of dealing between nations. It might well be that if scientists were to give a lead, others would follow. While it is manifestly not true that a common language ensures harmony between nations it certainly promotes clearer understanding, and at the present time there is nothing more urgently necessary than this.

Some factors governing the development of the earth's crust

V. V. BELOUSSOV

The mechanisms governing the movements of the earth's crust are exceedingly complex. Nevertheless sufficient order can now be seen in them to allow some understanding of how the earth's crust has reached its present form; to make some deductions useful to mining geologists and others concerned with immediate practical problems; and even to predict changes likely to occur in future ages. These problems are engaging the attention of geophysicists throughout the world, but this review is particularly concerned with research carried out in the field and with models in the Soviet Union during the past twenty years.

Everyone knows that the earth's crust is not at rest. It is always in motion, rising slowly in some places and sinking in others; sudden movements are expressed in earthquakes. The variety and complexity of crustal movements, and the laws that govern them, however, are apparent only to specialists. Such tectonic movements of the crust reflect the internal life of our globe, but this life is still very inadequately understood. The study of these movements, their variety, sequences, and mutual relations, is one of great scientific interest. Strangely enough, processes taking place in the depths of distant stars are in some ways better known to us than occurrences in the interior of our own planet. At the extremely high temperatures and pressures which prevail in the interiors of stars, matter undergoes such profound alteration that its properties are simplified and become amenable to mathematical idealization. Inside the earth, however, while the conditions are such that we must assume that they modify the properties of matter, they are undoubtedly different at different depths, and the molecular and atomic bonds are not completely disrupted. It is therefore very difficult to establish the properties of matter in the interior of the earth, at least so long as it remains impossible to reproduce the conditions experimentally.

The laws controlling the movements of the earth's crust must be taken into account in speculations concerning the processes taking place inside the earth and in the formulation of theories of mountain-building and of the origin of earthquakes. In dealing with this last topic, a knowledge of tectonics has a practical importance, since it provides a basis for working out methods of forecasting the time and place of earthquakes.

A knowledge of the factors governing tectonic movements acquires a still greater practical importance as a result of the way in which the present structure of the earth's crust has been built up. The distribution of sediments, the extent, composition, and thickness of these sediments, and the disposition of folds and faults appear to represent the sum of the effects of past tectonic movements. Knowledge of the history of these movements enables us to predict the arrangement and shapes of the masses of different rocks. Certain types of mineral resources are associated with particular rock-types or with particular structures such as folds or faults. The principles governing the tectonic development of the crust therefore provide the basis for many means of estimating the distribution of mineral resources, and of constructing metallogenetic charts, maps showing the probable distribution of oil-bearing strata and coal seams, and so on.

The branch of geology concerned with the causes and effects of movements in the earth's crust is known as geotectonics. This science has been extensively pursued in the Soviet Union during the last fifteen or twenty years, in both its theoretical and its practical aspects. Some fundamental contemporary ideas on tectonics are briefly set forth below. This article deals with the tectonic processes which are taking place, or have taken place, in those parts of the earth's crust that make the continents; it does not deal with the structure and development of oceanic basins. The author's account is based mainly on the results of Soviet investigations, and to some extent on his own work.

Study of the earth's crust shows that it undergoes various kinds of movements. Several schemes

for the classification of these movements have been proposed, but we shall confine ourselves to the simplest of them, classifying movements as oscillatory, fold-forming, and fault-forming. Movements of the first type result in slow elevation or depression of the crust; the second type results in the crumpling of beds into folds, and the third in the formation of structural breaks or faults.

These types of movements are not all of equal significance. The oscillatory movements are of fundamental importance. They occur throughout the earth's crust and serve as a background against which folds and faults are produced in some places during some periods of time. There are grounds for suggesting that oscillatory movements are the basic cause of fold-forming and fault-forming movements.

OSCILLATORY MOVEMENTS

Oscillatory movements which are taking place today can be studied most accurately by geodetic methods, for example by repeated accurate levelling. The effects of movements which took place within historical times can be established by the evidence of towns inundated by the sea as a result of sinking of the land, or of ports set back from the sea by uplift of the land, and so on.

Geology is concerned in the main, however, with the oscillatory movements which took place in former geological periods. These movements left their traces in the crust in the form of sedimentary deposits whose composition and thickness varied from place to place.

The sedimentary strata which are found in the continental areas are deposits laid down either in shallow water or on low-lying land such as deltas and coastal plains. Evidently, deep-water oceanic basins have not in general occupied the site of these continental platforms. Of the deposits formed on dry land, only those accumulating in low-lying regions have survived, those deposited on higher ground (for example, in river valleys) were as a rule rapidly eroded away by the action of water. The accumulation and retention of sediments are in themselves always evidence of the subsidence of the earth's crust. Thus, the parts of the crust where sediments have accumulated must have been regions of subsidence at the time of accumulation.

The composition of deposits depends to a considerable extent on what was going on at the time of accumulation in neighbouring regions which were being elevated. If uplift took place rapidly and with considerable force, these regions were subjected to rapid erosion and large quantities of coarsely broken up material were carried from them to the subsiding regions. If uplift was slow, then erosion was sluggish and only a little sludgy material was carried away, to be deposited on the periphery of the regions of subsidence. The remaining, larger, parts of these regions were filled up with organic deposits of local origin, predominantly limestone. Thus, by determining the distribution and composition of sedimentary strata of various ages it is possible to assess the former distribution of regions of subsidence and uplift, and to estimate the relative rate of uplift.

Further information can be gained by measuring the regional variations in the thickness of deposits of a particular age. For example, the Jurassic deposits in the centre of the Russian lowland have a thickness of the order of tens of metres, whereas those of the Caucasus reach a thickness of some thousands of metres. It has been established that shallow sea and lowland continental deposits accumulate to the extent that the subsidence of the crust allows, and that their thickness corresponds closely with the final amount of subsidence. Thus it is possible to separate out zones of greater and less subsidence within regions of deposition. The example mentioned above shows that during the Jurassic period the crust subsided both in the Russian lowland and in the Caucasus, but the amount, and hence the rate, of subsidence was considerably greater in the second region than in the first.

These and other methods have been used to study the history of oscillatory movements in various regions. In the Soviet Union work of this kind has been carried out on the Russian platform, in the Caucasus, the Crimea, Tien-Shan, Kopet-Dag, the Urals, and many other regions. In the course of this work some of the factors governing the development of oscillatory movements have been determined, and these will now be briefly discussed.

When oscillatory movements are taking place, the earth's crust is always divisible into regions of subsidence and uplift. Some general periodicity can be observed in the sequence of these movements; at some times uplift predominates in all areas and at others subsidence predominates everywhere. This fact enables us to recognize geotectonic cycles in the history of the earth. Each cycle begins with a phase of predominant uplift in which the area of dry land reaches a maximum, the relief is high and the seas are shrunken; further development leads to a phase of

predominant subsidence in which the dry land shrinks and becomes lowland, while the seas expand. The cycle finishes with a renewal of uplift and a shrinking of the seas. A new cycle then follows, with the same sequence as before.

This 'breathing in and out' of our planet is one of its most remarkable characteristics. The major cycles are of very long duration—a rough estimate is of the order of 150 million years. The best-known cycles are the last three which are called the Caledonian, Hercynian (or Variscan), and Alpine. The first of these covers the Cambrian, Ordovician, and Silurian periods, the second the Devonian, Carboniferous, and Permian and the third the Triassic, Jurassic, Cretaceous, Palaeogene, Neogene, and Quaternary. The periodicity of the oscillatory movements controls the recurrence of strata of similar composition in the stratigraphical succession (figure 1). Since certain mineral resources are associated with particular types of sediment, the same periodicity determines the distribution of these resources. Thus, for example, two large reserves of oil and coal are known in the earth's crust; one of them is associated with the Carboniferous system, the other with the Palaeogene (figure 2). The principal sources of salt, gypsum, etc., are the Silurian, Permian, and Neogene deposits. The last or Alpine cycle exhibits some irregularity in its development. The transitions from one phase of this cycle to the next took place at different times in the Pacific region (East Asia, the west of North America) and in the Atlantic region (Europe and the east of North America).

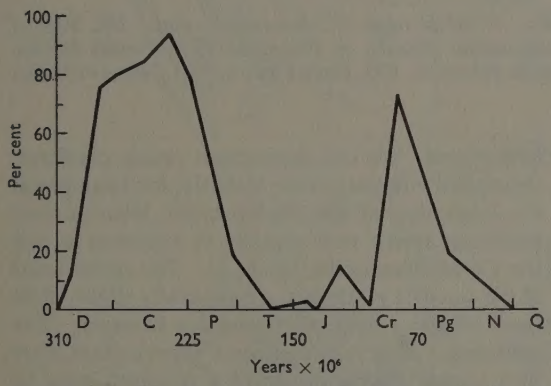


FIGURE 1 – *Percentage change of limestone content in the middle of other rocks on the Russian platform during the Hercynian and Alpine cycles (according to A. B. Ronov).*

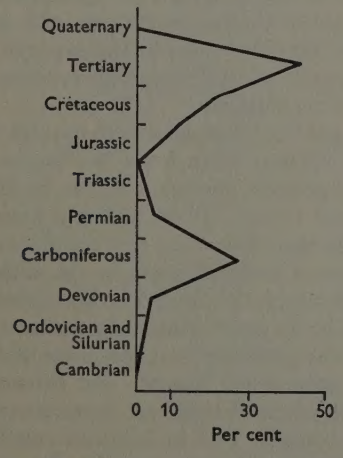


FIGURE 2 – *Distribution of world petroleum resources according to geological systems (according to I. M. Gubkin).*

An interesting feature of the oscillatory movements is their complexity: movements of different orders are always superimposed one on the other. Subsidence is complicated by local or partial uplift, and elevation by partial subsidence. The mutual superposition of movements of different orders, which are obviously governed by processes taking place at various depths in the earth, makes it possible to express, say, a particular uplift either as absolute—that is, as a raising of the earth's surface relative to sea level—or as relative, taking, for example, the form of a subsidence less pronounced than that of surrounding areas. If a partial uplift takes place in a region of general subsidence, the final result will obviously be the algebraic sum of both movements. In periods of general subsidence, uplift will usually be only relative, whereas in periods of general uplift it will be absolute.

During the last three cycles, and probably also during the preceding three or four cycles, the continental masses were divided into regions of two types—geosynclines and platforms. Geosynclines are characterized by extraordinarily intense and opposing oscillatory movements. They always consist of narrow elongated zones in which differential movements of opposite sense and high velocity take place, the velocity reaching a few millimetres or sometimes a few centimetres per year when averaged over a long period. In belts of subsidence occupied by the sea, sedimentary strata of very great thickness (up to 10–12 km) accumulate and uplifted zones take the form of island mountain ridges. At the end of a tectonic cycle, in the phase when uplift predominates over subsidence, high mountains are formed on the site of geosynclines. The disposition of regions of elevation and subsidence does not remain constant throughout a tectonic cycle. Uplifted regions appear within areas of subsidence; the residual

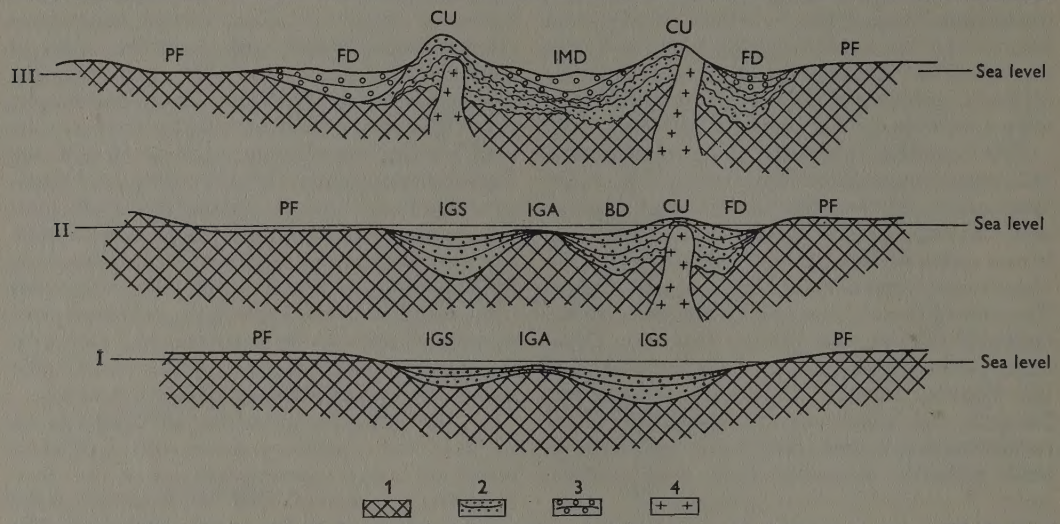


FIGURE 3 – *Schematic diagram of development of geosyncline. I. Initial stage. II. Intermediate stage. III. Stage of mountain formation. 1. Ancient sub-structure. 2. Predominantly marine deposits. 3. Predominantly continental deposits. 4. Granites. PF. Platform. FD. Fore-deep. IMD. Intermountain depression. CU. Central uplift. IGA. Intra-geanticline. IGS. Intrageosyncline. BD. Marginal depression.*

basins are gradually pushed aside like waves and encroach on former zones of uplift so that regions of uplift and subsidence often change places towards the end of a cycle (figure 3). The main Caucasian mountain range, for example, was raised in the Tertiary era from a region where one of the deep basins of the Caucasian geosyncline existed in the Mesozoic. The depression of the river Kura to the south of the main range was formed on the site of a much earlier uplift.

Platforms are characterized by feeble oscillatory movements of low velocity and small amplitude, with smooth transitions from regions of uplift to regions of depression. The distribution of elevated and depressed regions is considerably more stable than in geosynclines and changes less during a cycle, although the platform as a whole moves according to a general rhythm, first sinking and then rising.

In each cycle, the areas occupied by platforms increase at the expense of areas occupied by geosynclines. The earlier cycles are distinguished from the later ones by the more rapid growth of platforms and this has been one of the most important elements in the development of the crust, transforming the tectonic cycles from closed circles, as it were, into loops of a spiral.

Since in each cycle regions previously occupied by geosynclines became converted into platforms, the different parts of a platform may be of different ages. We can distinguish young platforms developed comparatively recently, for example at the beginning of the Alpine cycle, from ancient platforms which were already in existence in, say the Caledonian cycle (figure 4). The movements of the ancient platforms are generally slight while those of the young platforms are stronger. The conversion of a region from a geosynclinal state into a state characteristic of a platform may be such a gradual process that it is expedient to recognize an intermediate stage in which the region can be said to form a parageosyncline. The Russian and Siberian platforms are examples of ancient platforms, while the western part of Europe, north of the Alpine geosyncline, represents a recent platform.

These considerations lead us to inquire what the earth's crust may have been like in the earliest geological periods, and what it may be like in the very distant future. If the changes have always gone in the same direction, and continue to do so, then it seems probable that in the distant past there were no platforms and in the distant future there will be no geosynclines. In the most ancient periods, it is probable that platforms were either small or completely absent, and intense movements took place everywhere. Some investigators, however, consider that in Archean eras the crust was in some special state to which the concept of geosynclines and platforms did not apply. So far

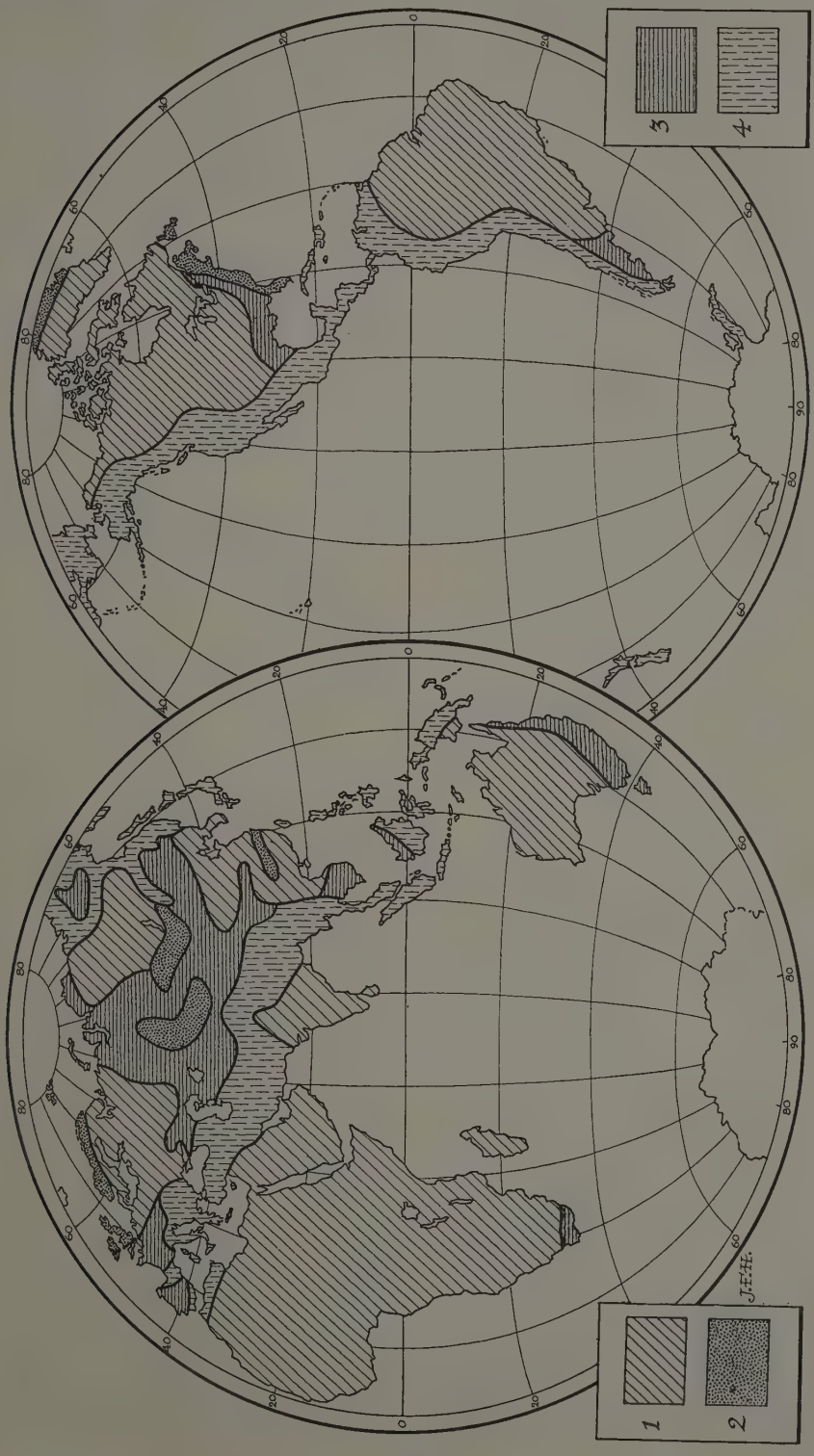


FIGURE 4 – *Tectonic scheme of the earth.* 1. *Ancient platforms.* 2. *Platforms on Caledonian folded base.* 3. *Platforms on Hercynian folded base.* 4. *Existing Alpine geosynclines.*

as the future is concerned, we have more justification for suggesting that when universal platforms have developed, the crust will enter on an entirely new phase of evolution.

The character of this phase is at present suggested by conditions in central Asia and in parts of Tien-Shan where the high ranges of the Tien-Shan are separated by deep inter-mountain hollows. In these regions, geosynclinal conditions had come to an end by the close of the Palaeozoic eras. Platform conditions existed there during the Mesozoic and most of the Tertiary, but in the late Neogene and Quaternary periods a new and intense series of tectonic movements began. The contrast between the uplifted mountain ranges and the intervening depressed hollows shows that vertical movements attained an amplitude of about 10 km over a period of several million years. We call this new stage in the development of the earth's crust the stage of activation of platforms. It has begun not only in Central Asia but also in southern Siberia (Altai, Sayansk Mountains), Africa (the region of the rift valleys) and some other regions. It shows that the platform is not the final product of tectonic development and that the 'sclerosis' which many authors have written about does not in any way threaten the earth's crust; the platform itself is an unstable structure and intense movements can recur after it has developed.

FOLDING MOVEMENTS

Folding movements, as we have already mentioned, are developed against a background of oscillations and are subordinate to them. Not very long ago, attempts were made to explain all types of folding of the crust in terms of horizontal compression produced by the shrinking of the earth. It is now clear to us that this line of approach is certainly incorrect.

It must be realized first of all that many diverse phenomena of varying significance are classified under the title of folding. The author, with a group of colleagues and students, is at present carrying out extensive studies of a series of regions of folding in the Soviet Union. The field studies are being supplemented by laboratory experiments which are carried out as far as possible under similar physical conditions.

The results of this work are consistent with the view that systems of folding can be divided into at least three types which differ in the mechanism or kinematics of their formation.

First of all there is block folding. This is a bending of strata as a result of vertical uplift or depression of discrete blocks of the earth's crust. The characteristic products are box folds with flat tops and steeply inclined limbs, but experiments with models show that when the block—which acts, as it were, as a die—lies at great depths, the strata near the surface form domes instead of box folds. The development of box folds is in many instances associated with oscillatory movements. The history of a block fold, as revealed by its structure, often indicates that it grew slowly throughout whole geological periods and was not infrequently subjected to alternating upward and downward movements. The connection with oscillatory movements, which is a genetic one, is very close; we can recognize actual oscillatory movements in box folds, but they are on a small scale.

The second category of folding is folding due to differential loading. This results from the horizontal displacement of material in a layer which becomes highly plastic at depth. As a consequence of this displacement, the plastic layer becomes thin in the region from which the material flows and is thickened at the place into which it is injected. The overlying strata sag above the place from which the material migrated and are raised up over the thickened region. Sometimes the injection has such a pronounced effect that 'cores of penetration' are formed. The peculiarity of this kind of structure is that it does not continue in depth. Below the plastic layer, which plays the active role in folding, the rocks may all lie horizontally, or may be deformed in an entirely different way.

A lack of uniformity in the load resting on the plastic layer, and a low specific gravity in this layer relative to that of the overlying rocks are the main causes of horizontal flow in subsurface plastic material. If the depressions produced by vertical movements are filled up by sediment and the uplifted regions are eroded, the load on the plastic layer becomes uneven. Equilibrium is disturbed, and the plastic material may begin to flow from the depressions towards the uplifted regions. A reversed relief, with high ground over tectonic depressions and lower ground over uplifted regions, may contribute to this process. It is also favoured by low specific gravity of the plastic rocks which makes them tend to move upwards from beneath the heavier overlying beds. This last factor acts independently during the formation of what are known as diapiric domes, in which a core of light salts or gypsum slowly floats up like

a very viscous liquid through heavy sands or clays overlying it. Folding due to differential loading may complicate block folding in regions where there are thick plastic layers in the succession.

The final type of folding is a general crumpling produced in parts of the earth's crust where longitudinal flexures are developed under the influence of horizontal compression.

The causes of horizontal compression should not, as our investigations have shown, be sought in world-wide processes. It is fundamentally much sounder to seek these causes in more local processes, particularly those related to geosynclines where general folding predominates. Opposed oscillatory movements often result in the division of the crust into blocks, and the slopes connecting uplifted and depressed blocks produce a step-like structure. When blocks are raised above their surroundings, the upper parts tend to slip outwards, setting up a pressure on neighbouring lower-lying blocks whose strata are thus crumpled. An isolated elevated block acquires a mushroom-shaped section and exerts a pressure on the blocks on either side. Where blocks follow one another step-wise, every block presses on the one below it. The blocks thus crumple one another in succession, with the exception of the uppermost, whose structure would appear as a simpler one.

Other local causes of general folding can also be related to opposed oscillatory movements: for example, if a certain block first rises and then sinks, the strata covering it will be stretched during the period of uplift and then thrown into folds when the block sinks again. Multiple oscillatory movements produce more numerous and more complex folds. Other examples of factors producing general folding could be mentioned; they all have in common the fact that they are related to opposed vertical movements in the crust. General crumpling therefore occurs predominantly in geosynclines.

The mechanical causes of the outward slipping of the upper parts of raised blocks are twofold. In the first place, there is the simple effect of gravity; in the second, there is the squeezing out of material from within the crest of the rising block as a result of the resistance set up by the overlying strata. Both processes are easily reproduced in models.

Until recently, geologists who were brought up on survivals of the contraction hypothesis did not ask themselves about the causes of formation of folds in restricted areas, since they considered folding to be a general phenomenon capable of being interpreted only on a regional scale. Now, however, we need to establish the local cause of folding; this may vary from place to place, although, as has been shown already, it is generally related to opposed oscillatory movements in geosynclines.

The various types of folding are, as the previous pages suggest, connected in a systematic way with a regime of oscillatory movements. Block folding always occurs in platforms and in geosynclines. It is more intense in the latter, but as it appears to be the only type of folding which occurs in the former, its independent occurrence is, in general, characteristic of platforms. It is usually stronger in young platforms than in ancient platforms.

Folding due to differential loading requires the presence of thick successions containing layers of plastic rock. Favourable conditions exist in deep depressions on platforms where saliferous or gypsiferous layers are not uncommon in sedimentary successions. In these circumstances, folding most frequently produces diapiric domes. Still more favourable conditions exist in the fore-deeps which are located between geosynclines and neighbouring platforms. Here, the successions are even thicker, and may contain thick layers of salt, gypsum, or plastic clay. Not only diapiric domes but also elongated folds produced by injection, separated by wide sloping depressions, may be formed: this is known as coulisse-folding, and has the appearance of a comb.

Finally, the geosynclines themselves, deep depressions filled in by very heterogeneous rocks, provide conditions which are no less favourable for folding of the type discussed above. This type of folding is found in geosynclines, but is dominated by general crumpling and is not always distinguishable. For this reason, block folding in geosynclines does not attract the attention that it deserves.

General crumpling, as has been shown, demands differential vertical movements and hence it is associated as a rule with geosynclines, where it masks the appearance of other types of folding. It also occurs on a small scale in isolated regions and in platforms where differential movements take place locally, for example in deep rift valleys.

There is a definite relation between the place and time of development of general folding on the one hand, and the progress of oscillatory movements on the other. The folding begins on the flanks of blocks rising inside subsidiary depressions and encroaches on an ever-increasing area with the continued elevation of the blocks (figure 3).

FAULTS

Tectonic faults are formed where stresses in a rock exceed its strength. They develop under conditions of tension, compression, or shearing, for example when beds are arched up and thus tend to increase their area. Any uplifted mass has, to a greater or less extent, a tendency to be cleft by longitudinal, transverse, and radial cracks. The small blocks defined by these cracks are displaced upwards or downwards with the formation of normal faults. Under conditions of local compression, thrusts, strike-slip faults, and so on are formed in association with folds.

The behaviour of faults can be studied by means of models, and is explicable in terms of physical principles. These studies have served Soviet tectonicians as a basis for the development of the discipline known as tectonophysics, which is the application of physical methods and concepts to the investigation of the deformation of the earth's crust. The mechanism of formation of faults has been extensively studied in the Soviet Union; in particular, it has been found that many interesting features of faults arise from the fact that they are produced not by cracking but by viscous flow following plastic deformation.

Deep faults present a special problem which is a long way from being solved. There are grounds for supposing that at least some parts of the earth's crust are fractured by deep faults which penetrate even to the mantle. These faults, beginning as weakened scars, are made use of in the course of oscillatory movements. In addition, it is suggested that they have a systematic direction and determine the course of geosynclines and other tectonic complexes. Their formation is, according to some scientists, connected with changes in the form of the earth due to the slowing down of its rate of rotation.

It is certainly remarkable that, for instance, practically all the active tectonic zones in the region between Lake Baikal and the Crimea have the same north-west strike. These include zones of uplift and subsidence in the east and west Sayansk Mountains, the Altai, the Tien-Shan, central Kazakstan, Kopet-Dag, the Caucasus and the Crimea. Yet the same north-west strike is repeated by the junctions which separate zones of uplift and subsidence in the non-Alpine region of western Europe. Here the zones were clearly formed only at the beginning of the Mesozoic, since at the end of the Palaeozoic era the tectonic zones had a completely different strike.

The role of such deep faults in the structure of the earth and their history present an attractive problem for further study. This touches on the problem of large horizontal movements along deep vertical faults. American geologists are attracted by this topic, as illustrated by the San Andreas fault; Soviet geologists do not share their enthusiasm and in fact have strong doubts as to the reality of large horizontal displacements.

Another interesting problem which we have not touched on is the origin of continents and oceans. If we had turned our attention to this problem we might have drawn on material from geophysical sciences, but this is not within the scope of the present article. Still less can we deal here with the possible causes of tectonic movements, since this involves not only geophysical but geochemical considerations.

What has been said, so it appears to us, is enough to show how complex, and at the same time how systematic, are the mechanisms associated with movements in the earth's crust.

BIBLIOGRAPHY

BELOUSSOV, V. V. Общая геотектоника (General geotectonics). Moscow. 1948.

Idem. Основные вопросы геотектоники (Fundamental questions in geotectonics). Moscow. 1954.

Idem. Труд. Геофиз. Инст., No. 17, 144, 1952.

Idem. Советс. геол., No. 1, 1958.

GZOVSKIĬ, M. M. Извест. A.H. C.C.C.P., сер. геофиз., Nos. 5 and 6, 1954.

KOSYGIN, YU. A. Основы тектоники нефтеносных областей (Problems of the tectonics of oil-bearing regions). Moscow. 1958.

PEĬVE, A. V. Извест. A.H. C.C.C.P., сер. геол., No. 5, 1945.

SORSKIĬ, A. A. Труд. Геофиз. Инст., No. 18, 145, 1952.

TETYAEV, M. M. Основы геотектоники (Problems of geotectonics). Moscow. 1941.

KHANI, V. E. Геотектонические основы поисков нефти (Geotectonic problems in oil prospecting). Moscow. 1957.

The biochemistry of the eye related to its optical properties

ANTOINETTE PIRIE

Many of the experimental studies of the physiology of vision are concerned with the light-sensitive pigments of the rod and cone cells of the retina. These are essential for light reception, but so also are other parts of the eye such as cornea and lens. This article considers some aspects of the biochemistry and physiology of the parts of the eye through which light reaches the retina, dealing with the eye both generally and with reference to the specialized adaptation developed in some animals to assist their vision in poor light.

The theme of this article is the relation between the biochemistry of the eye and its function as a light-transmitting, rather than a light-receiving, organ. The rod and cone cells of the retina that contain the light-sensitive pigments and the neurones of the retina and the optic nerve are concerned with light reception and vision, while the rest of the eye—the refractile and transparent parts, such as the cornea, the lens, and the vitreous body—are essential for the transmission and focusing of light on to the light-sensitive cells. These parts of the eye (figure 1) must be both transparent and optically uniform—if the liver or the little finger grows by as much as a millimetre the change is not noticeable, but increase the length of the adult eyeball by a millimetre and abnormal vision is the result. Change in shape of any part of the eye because of a biochemical or pathological lesion can be disastrous for function. Ankles can and do swell in hot weather, but however uncomfortable this may be it is still possible to get about. But if the cornea swells even microscopically, because the respiration of its epithelial cells has been checked through lack of oxygen, vision is distorted and the discomfort of the eye is intolerable.

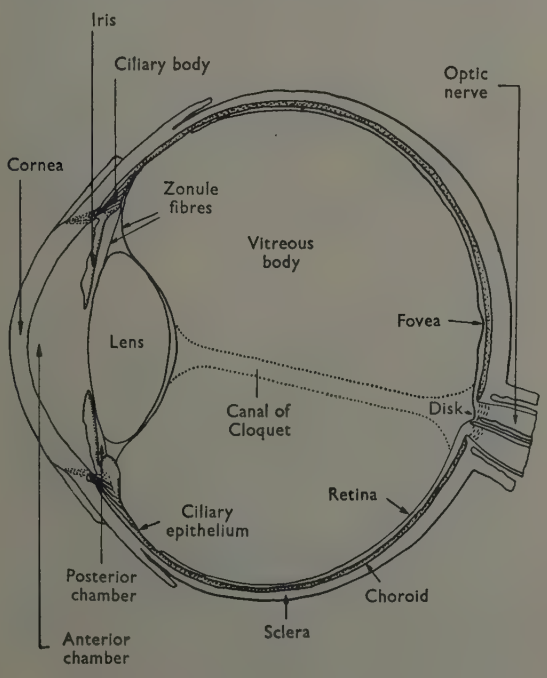


FIGURE 1 – *The human eye in section.*

Quite simple experiments show that the transparency and optical properties of cornea and lens depend on their metabolism. One such series of experiments analysed the visual difficulties produced by contact lenses.

The cornea, which is the transparent circular area of the outer coat of the eyeball, consists of three parts: the epithelium, which is made up of several layers of box-shaped cells; the stroma, which consists of interlacing collagen fibres with a few cells in the interstices (figure 4); and a single layer of endothelial cells on the inner surface. Now people who wear contact lenses may find that after a few hours their eyes start to irritate and they can no longer see clearly. Vision is blurred and distorted, and anything brightly lit appears to have a halo round it. Removal of the contact lenses restores normal vision. Examination of the eye when it is in its irritated state shows that some of the corneal cells are swollen, and it is these swollen cells that cause blurring and distortion by irregular refraction of the light rays.

G. K. Smelser [1–3] has investigated the problem both in guinea-pigs and also in himself. He

fitted the pigs with contact lenses and later examined the cornea both in the living animal and histologically, and found that wearing the lens caused swelling of epithelium with accumulation of fluid between the collagen fibres of the stroma. The glycogen granules of the epithelium disappeared and the lactic acid content rose, pointing to change from an oxidative to an anaerobic metabolism. So Smelser fitted contact lenses under which he could imprison a bubble of oxygen or a bubble of nitrogen and then investigated the state of the cornea after some hours' wear. Oxygen maintained the cornea in a normal state, while nitrogen allowed swelling. This was a direct proof that respiration of the corneal cells is essential to maintain visual function. The corneal cells are normally covered by a film of tears, and the oxygen of the air diffuses into them through this film. By using contact lenses that have one or two small holes near the edges so that tear fluid can seep in and out with the small movements of the contact lens on the eye, the epithelial cells can get sufficient oxygen and glucose to maintain both respiration and their proper shape and, hence, their visual function.

These experiments were carried out in the living animal. Other experiments, using excised eyes or corneas, show the same dependence of normality on metabolism. The cornea will swell if it is cooled or if, at normal temperature, it is deprived of oxygen or glucose, but the swelling can be reversed when the cornea is warmed and oxygenated in the presence of glucose [4]. Unfortunately we do not know the processes involved. We know that osmotic equilibrium is linked to respiration, but that is all.

Very similar experiments have shown that oxidative metabolism of the lens is necessary to keep it optically transparent and non-swollen. The lens, enclosed within its capsule, suspended by the radially placed zonular fibres, grows throughout life by adding new fibres to the outer edges and so pushing the old fibres to the centre (figure 2). Its function is to focus the light on to the retina, and to do this it must maintain its clarity and its elasticity throughout life. The metabolic processes that go on in the lens are essential for this. Not only does it, like the cornea, gain water and sodium and lose potassium when cooled or subjected to lack of oxygen or glucose, or when exposed to metabolic poisons such as iodoacetic acid or cyanide [5], but the lens becomes cataractous when its metabolism is upset in life. Cool a mouse down, and the lens becomes opaque. Cool down the excised eye of a calf or young rabbit, and the same thing happens. Deprive a rat of oxygen, and bilateral cataracts will appear. Such lens opacities are reversible and disappear when the animal is warmed or when oxygen is restored; but most lens opacities are irreversible, and may lead to almost complete blindness.

Most of the energy of metabolism in the lens is supplied by the glucose of the aqueous humour [6]. This fluid is formed by the ciliary body, circulates over the lens, and leaves the anterior chamber by flow down the canal of Schlemm, which connects the aqueous humour with the veins, and by diffusion through the iris and cornea. Glucose reaches the lens by this circulation of fluid, and most of it is broken down in the lens fibres to lactic acid, which then diffuses away. And, as one might expect, upset of glucose metabolism is associated with formation of cataract.

Diabetic cataract is known in man, and can be produced in experimental animals by cutting out the pancreas or by injection of alloxan or dehydroascorbic acid, which induce permanent diabetes. Cataracts can also be produced within a matter of days in young rats by feeding excessive amounts of sugars such as galactose or xylose (figure 3), and a description of biochemical changes in such cataracts exemplifies the inter-relation of normal metabolism and normal function in the lens.

Let us consider the case of babies first. Some babies have an inborn error that prevents them from metabolising the galactose moiety of the lactose in milk. They do not grow well and they develop cataracts. The galactose they cannot metabolise accumulates in the blood and is excreted in the urine. This inborn error is termed galactosaemia. It is possible to locate the break in the galactose metabolic chain and to show its relevance to the biochemistry of the eye.

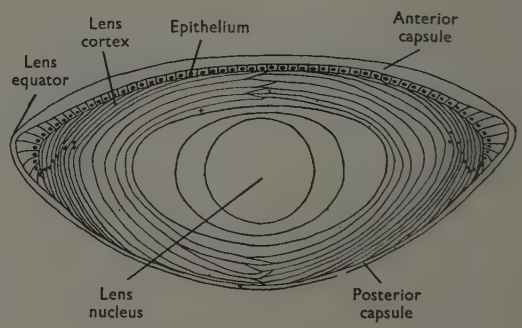


FIGURE 2 – *The lens in section.*

FIGURE 3 – *Galactose cataract in the rat.*

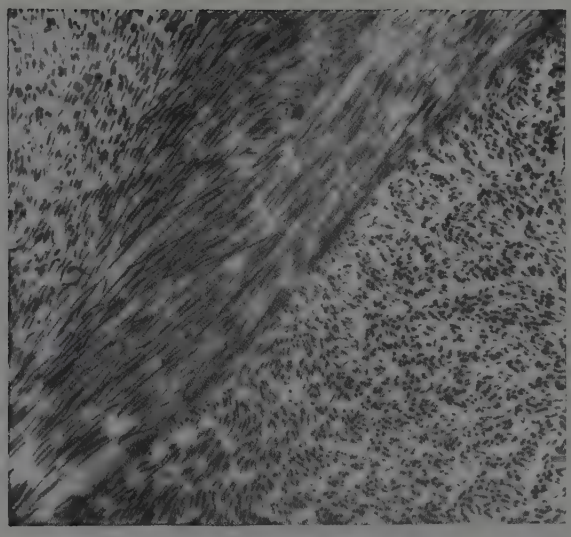


FIGURE 4 *(right)* – *Electron micrograph of interlacing bundles of collagen fibres in the cornea* [22]. (×7150)

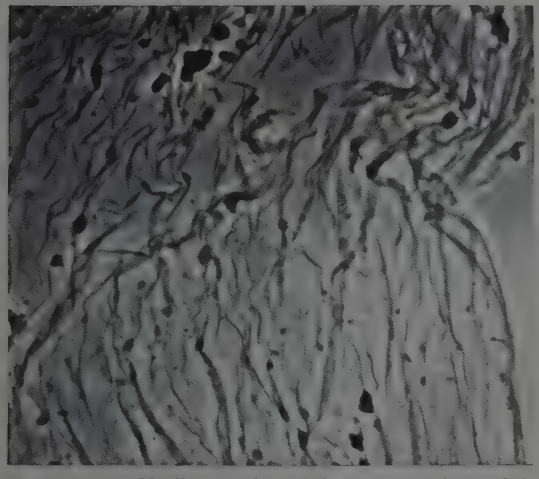


FIGURE 5 – *Hyaline membrane of the vitreous body of the ox. (Phase contrast,* ×700)

FIGURE 6 – *Coarse fibres of the vitreous body of the rabbit. (Phase contrast,* ×700)

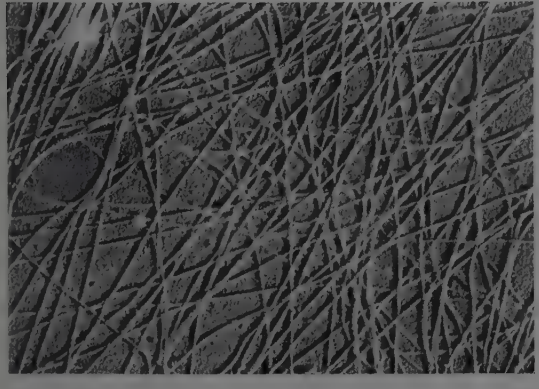


FIGURE 7 – *Electron micrograph of fine collagenous fibres of the vitreous body of the ox* [17]. (×31 000)

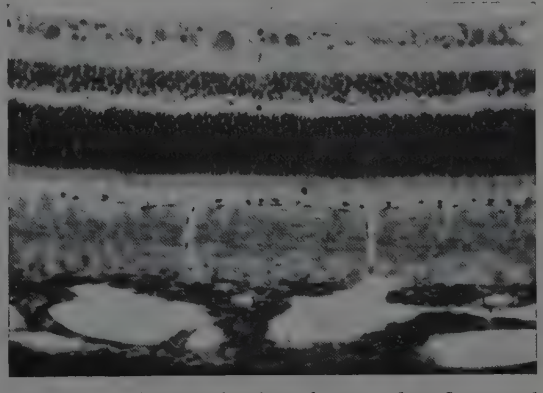


FIGURE 8 – *Section of retina of cat to show flat tapetal cells.* (×130)

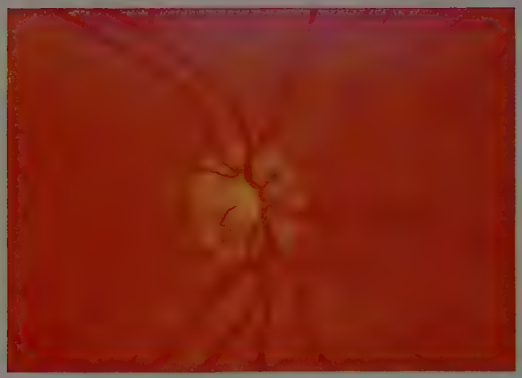


FIGURE 9 – *Human retina seen with ophthalmoscope.*

FIGURE 10 – *Cat retina seen with ophthalmoscope, showing tapetum.*

FIGURE 11 – *Opened eye of cat to show tapetum.*

FIGURE 12 – *Guanine crystals in choroid of dogfish, viewed under polarized light.*

FIGURE 13 – *Crystals in tapetum of dog. Section viewed under polarized light.*

FIGURE 14 – *Open eye of ox, showing retina and tapetum.*

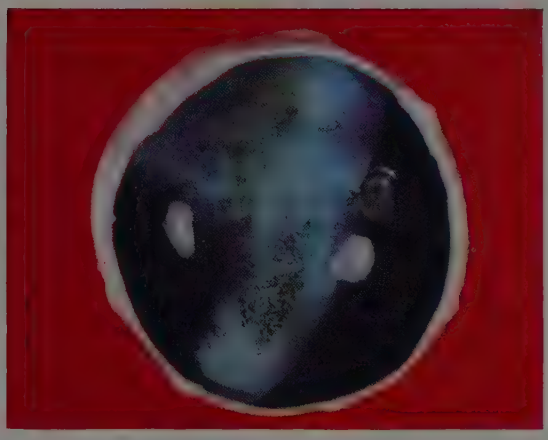


FIGURE 15 – *Open eye of ox with retina removed.*

FIGURE 16 – *Guanine crystals in retinal tapetum of alligator* (Alligator Mississippiensis).

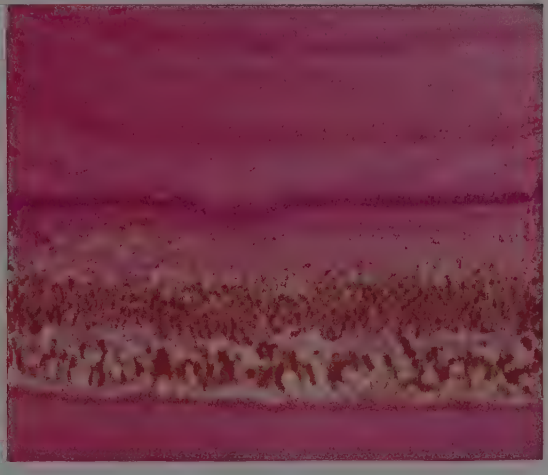


FIGURE 17 – *Guanine crystals in retinal tapetum of bream* (Abramis brama).

FIGURE 18 – *Section of iris of carp, showing guanine crystals on front surface, viewed under polarized light.*

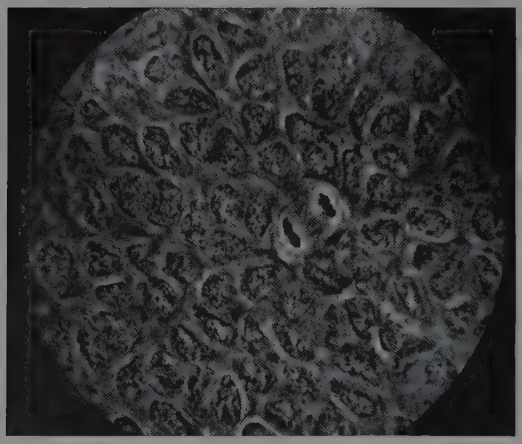


FIGURE 19 – *Normal lens epithelium, showing a normal mitosis.*

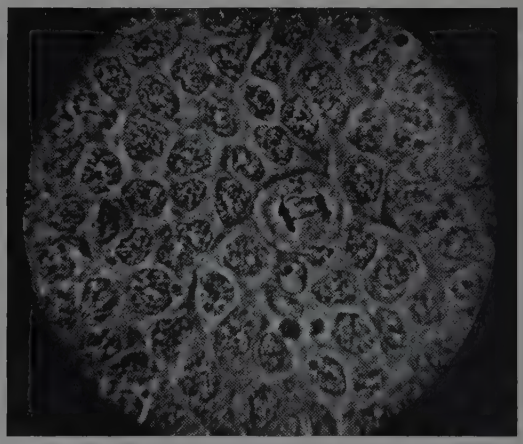


FIGURE 20 – *Epithelium from lens irradiated 14 days earlier. Note one abnormal mitosis and several fragmented cells.*

The first stages of galactose metabolism are considered to be these:

$$\text{ATP} + \text{galactose} \rightarrow \text{galactose-1-phosphate} + \text{ADP}$$

$$\text{galactose-1-phosphate} + \text{UDPG} \rightleftharpoons \text{glucose-1-phosphate} + \text{UDP gal}$$

$$\text{UDP gal} \rightleftharpoons \text{UDPG}$$

There is an accumulation of galactose-1-phosphate in the red blood corpuscles of galactosaemic infants [7], and haemolysed red blood cells from such infants cannot form UDP gal from UDPG and galactose-1-phosphate [8]. Galactosaemia therefore seems to be a congenital deficiency of the enzyme that catalyses this reaction. This enzyme is normally present in tissues, including presumably the lens, as galactose can be broken down to lactic acid by cattle lens *in vitro* [9].

Investigation of the metabolism of galactose in the lens of the galactose-fed rat shows that the normal lens contains only traces of galactose and galactose-1-phosphate. This is true also of the lens of the galactose-fed rat before opacity develops, but when the lens develops a cataract there is accumulation of galactose-1-phosphate in the lens capsule and epithelium [10]. It is suggested that this substance inhibits the normal breakdown of glucose by the lens and so causes development of opacity.

There are many other ways in which lens opacities may be produced in experimental animals, and metabolic studies of such partly or totally opaque lenses have shown that loss of adenosine triphosphate, loss of glutathione, and finally loss of soluble protein is a common phenomenon. But it is very difficult to know what starts off such degenerative changes. In an attempt to find out, we have studied development of X-ray cataract in rabbits, exposing one eye to the X-ray beam and using the lens of the other eye as a normal control [11–13]. No change is visible clinically in the lens for quite a long time after radiation. After our standard dose of 1400 r, the lens of a six-month rabbit may appear normal clinically for several months, though it will almost certainly be completely opaque eight months to a year after irradiation. In a younger rabbit the process is greatly accelerated; in an older one, complete opacity may never occur.

While these clinical changes are taking place it is easy to show changes in constituents and in the activity of enzymes in the lens by comparing the irradiated lens with the normal lens of the other eye. In this way we can show that there is a progressive diminution of glutathione, of glutathione reductase, and of the enzymes that synthesize glutathione from its constituent amino acids. The earliest change we have found is diminution of glutathione, and we have used this as a yardstick against which to measure other changes. There is a falling off in the activity of glyceraldehyde phosphate dehydrogenase, of aldehyde oxidase, and of glyoxalase; proteins are synthesized at a lower rate; finally there is actual breakdown of lens proteins. As with other forms of cataract,

[1] ATP = adenosine triphosphate
ADP = adenosine diphosphate
UDPG = uridine diphosphoglucose
UDP gal = uridine diphosphogalactose

there is loss of high-energy phosphates, such as adenosine triphosphate. On the other hand, some enzymes are practically unaffected. Hexokinase, which catalyses the phosphorylation of glucose, aldolase, which splits hexose diphosphate to triose phosphates, and lactic acid dehydrogenase, which are all enzymes concerned with glycolysis, and also oxidative enzymes such as *iso*citric dehydrogenase, the malic enzyme, and cytochrome reductase, are still active in the opaque lens or lose activity at a very late stage.

But these changes in constituents and enzymes are not detectable for some time after irradiation. It may be days, weeks, or even months, depending on the age of the rabbit and the dose of radiation, before diminution of glutathione or loss of high-energy phosphate can be detected. This delay in onset suggests that these changes are secondary and that radiation is doing something we have not yet detected. In an attempt to analyse this we have begun a histological examination of the lens.

Radiation is known to damage cells capable of division more readily than others. In the lens, the dividing cells are concentrated in a ring just anterior to the equator, and it can be shown that if a beam of X-rays is passed through the core of the lens, thus missing the dividing cells, no opacity of any kind will ensue, but if the core is shielded and the whole periphery of the lens is irradiated a complete cataract will result [14]. Thus radiation damages only those cells at the periphery—probably, by analogy with other tissues, those epithelial cells capable of division. These constitute an extremely small proportion of the total lens mass, yet are of prime importance for lens function (figures 19 and 20).

A further point, which may be of general interest, has also emerged. We found that if a small part of the periphery of the lens was shielded the lens opacity produced was trivial, while if the total periphery was irradiated total opacity developed. A small area of healthy dividing epithelium therefore has a very great effect in maintaining lens structure. We are now trying to see what kind of repair process this is by irradiating one half only of the lens and microscopically examining flat preparations of the epithelium at different times afterwards in order to see whether a migration of cells from the non-injured to the injured side takes place.

All this is very far from being detailed biochemistry. Radiation injures the dividing epithelial cells; as a consequence the growth of the lens is impeded, there is actual loss of epithelial cells, and those remaining, many of them damaged, cannot maintain the inner fibres. At a certain stage these begin to decay, and at this point one can detect enzymic and other changes in the lens as a whole. But one still has to find out what the injury is in biochemical terms.

THE VITREOUS BODY

Let us now go deeper into the eye and consider the vitreous body, the last stage in the path of the light ray to the retina. This jelly fills the space between retina and lens. Mörner in 1896 demonstrated that the vitreous body of the cow contained collagen (the main fibrous protein of the skin), but this was forgotten and for many years it was taught that it was structureless. We have now come full circle and find an embarrassingly large number of diverse fibrous and membranous structures to be present, some of which resemble collagen and some of which do not (see figures 5–7) [15–17].

The vitreous body can easily be separated by filtration or centrifugation into two parts, the soluble vitreous humour and the insoluble fibrous residue. The fibrous residue of the vitreous body is complex—the main part is made up of a meshwork of very fine collagenous fibrils (figure 7) which are surrounded by a hyaline membrane (figure 5). The whole structure is anchored to the retina by coarser fibres which spring from the area of the retina just behind the lens (figure 6). The vitreous humour, which is viscous owing to the presence of a mucopolysaccharide, hyaluronic acid, permeates the whole mass.

How can one relate this structure to the behaviour of the vitreous body during life? Two troubles in the eye which affect vision, and which are directly or indirectly concerned with vitreous structure, are partial liquefaction of the vitreous body with formation of opacities, and retinal detachment.

When you look at a blank wall or a clear sky you frequently see small floating grey or black dots or threads which, if your eye is still, gently move across your field of vision. These 'floaters', as they are called, are present in nearly everyone's eyes and are little tags of fibre in the vitreous body. They move because the vitreous body is not rigid. They move very slowly and only for small distances because it is a viscous jelly.

These small fibrous knots and remnants are normal, but if the fibrous network of the vitreous body gets disorganized, either through its own partial liquefaction or through depolymerization of the hyaluronic acid, serious opacities develop.

A still more serious threat to vision is detachment of the retina. Here a part of the retina tears or floats off and so becomes useless as a light-receiving mechanism. I think it is generally considered that at least some types of retinal tears and detachments are due to traction on the retina by vitreous fibrils. The retina is most firmly attached to the vitreous body at the base, near to the ciliary body, and it is here that retinal degeneration and detachment most frequently take place.

One might say that, both in the case of vitreous opacities and in retinal detachment, digestion of the fibres of the vitreous body by an enzyme injection might be helpful. Unfortunately collagenase, which will certainly liquefy the vitreous body both *in vitro* and *in vivo*, will also dissolve the collagen in the retinal blood vessels, and injection of collagenase into the vitreous body can cause retinal haemorrhages. Again, although collagenase liquefies the main vitreous body it does not digest the fibres which most firmly attach it to the retina at the anterior edge. These fibres (figure 6) are not collagen. It is not known what class of fibrous protein they belong to or whether they are unique. It might be that if we could digest these fibres—they are susceptible to trypsin—we might modify a retinal detachment, but until we know a good deal more of their chemical nature we cannot attempt to modify them *in vivo*. But on the whole the vitreous body behaves admirably. It is 99 per cent water, it is almost optically clear, but yet sufficiently rigid to hold the eyeball in shape and the retina in place; its chemistry is adapted to its function.

I have, of course, in writing throughout of the eye, extensively oversimplified, because there is in fact no such thing [18]. The eyes of different members of the same species differ in their details, and there are striking differences between the eyes of, say, cats, and bulls, and fish. All differ from one another, both in construction and in performance. Performance is very difficult to judge, because the eye and the brain form a unit for this purpose. A consideration of structure leads us into some very peculiar biochemistry, and to demonstrate the startling differences that exist between the eyes of different animals I can do no better than describe the chemical adaptations which are the basis of eye 'mirrors'.

ADAPTATIONS IN CHOROID AND RETINA TO FORM A REFLECTING SURFACE

When one is out at night with a torch or in a car one can often see the glowing eyes of a cat or dog reflecting the light back at one. Many mammals and fishes reflect light in this way. Birds' eyes in general do not, nor do ours. In our eyes the retina is backed by a uniformly black choroid which simply absorbs all light which reaches it. Light reflected from the human retina is reddish and comes from the retina itself and its blood vessels (figure 9). But many animals (figures 11, 14, 15) have a special area of choroid or retina, called a tapetum lucidum, which acts as a mirror, so that light which falls on it is reflected through the overlying retinal cells again [18]. Obviously this cannot increase visual acuity but could be useful in raising the sensitivity to dim light, since any light not absorbed on its first passage through the retina might stimulate the light-sensitive cells as it traversed them again after reflection.

The tapetum lucidum in the dog or cat is a triangular area in the upper half of the eye which, when viewed in life (figure 10) or in the excised eye (figure 11), appears as a blue-green glistening area. In microscopical section it can be seen that the pigment epithelial cells of the retina contain no pigment in the tapetal area and are backed by several layers of large flat cells in the choroid (figure 8). These cells are full of crystals (figure 13). Recently it has been found that the crystalline material laid down in the tapetum of carnivores such as the dog, cat, badger, seal, and fox is a complex of zinc with the sulphur-containing amino acid cysteine [19]. The cells of the tapetum of the silver fox contain 16 per cent of their dry weight as zinc and 8–9 per cent as sulphur.

That this tapetal area is essential for visual function is suggested by the fact that if a dog is injected with a metal chelating agent such as dithizone the eye shine is abolished, the animal becomes blind as the tapetum degenerates, and the retina becomes detached. Dithizone is frequently used to produce diabetes, as it causes degeneration of the islets of the pancreas (again probably owing to removal of zinc), but the dose required to cause visual changes in dogs is lower than the dose necessary to produce diabetes. No repair seems to take place in the eye after removal of zinc cysteine [20].

Many fish, amphibia, and reptiles also lay down crystalline material, not only in their choroid but also in their iris (figures 16–18), where again it acts as a reflector. These crystals are made up of the purine guanine, which is also the substance that gives fish scales their silvery appearance; it is indeed known as 'fish silver'. In the dogfish, *Squalus acanthias*, the guanine crystals are

very large and arranged in a regular way, apparently at an angle of 45° to the visual cells (figure 12). In dim light they are uncovered, but in bright light they become covered with pigment which migrates to and fro according to the light, thus increasing the range of light intensities that the eye can respond to.

Herbivores such as cattle and sheep have modified their choroid rather differently, but also to form a mirror. In these animals the choroidal tapetum is made up of fine parallel fibres which act as a diffraction grating and reflect coloured light in the same way as the wings of some butterflies. The choroid has a high concentration of barium, a metal which is practically absent from all other parts of the body but which may reach 120 mg/100 g dry weight in the choroid of the cow [21]. We do not know whether the barium is connected with the tapetum.

The basic mechanism of vision lies in the light sensitivity of the pigments in the rods and cones of the retina. Added to this there is the interaction between eye and brain so that the image received on the retina may be interpreted. Optically the eye of the bird is in many ways superior to the eye of man, but one can hardly doubt that the range of visual experience of the bird is less than that of man owing to the relative simplicity of its brain.

The whole eye is adapted to the purpose of forming a clear image on the retina. We have seen that the efficiency of the light-transmitting and light-focusing parts of the eye—the cornea, the lens, and the vitreous body—is dependent both on metabolism and chemical structure, and we have seen that extraordinary chemical specializations take place in the choroid in order to increase the range of light intensity to which the retina can respond. Each separate structure in the eye has a part to play, and normal light reception depends on the normality of each part.

ACKNOWLEDGMENTS

I have much pleasure in thanking three photographers. Mrs M. Overall of the Nuffield Laboratory of Ophthalmology for the preparation of the diagrams of the eye, Mr Allen of the Oxford Eye Hospital for the picture of the human fundus and that of the cat, and finally Mr Blackwell of the Department of Human Anatomy, who has taken very great trouble and care in producing all the other colour photographs as well as some of the black and white ones. Dr N. Ashton very kindly supplied the photograph of the section of the cat retina.

REFERENCES

[1] Smelser, G. K. *Arch. Ophthal., Chicago*, **47**, 328, 1952.
[2] Smelser, G. K. and Ozanics, V. *Ibid.*, **49**, 335, 1953.
[3] Smelser, G. K. and Chen, D. K. *Ibid.*, **53**, 676, 1955.
[4] Davson, H. *Biochem. J.*, **59**, 24, 1955.
[5] Harris, J. E., Hauschildt, J. D., and Nordquist, L. T. *Amer. J. Ophthal.*, **38**, 141, 148, 1954; **39**, 161, 1955.
[6] Pirie, A. and van Heyningen, R. 'The Biochemistry of the Eye'. Blackwell Scientific Publications, Oxford. 1956.
[7] Schwarz, V., Golberg, L., Komrower, G. M., and Holzel, A. *Biochem. J.*, **59**, xxii, 1955.
[8] Kalckar, H. M., Anderson, E. P., and Isselbacher, K. J. *Biochim. Biophys. Acta*, **20**, 262, 1956.
[9] van Heyningen, R., in Pirie, A. and van Heyningen, R. [6].
[10] Schwarz, V. and Golberg, L. *Biochim. Biophys. Acta*, **18**, 310, 1955.
[11] Pirie, A., van Heyningen, R., and Boag, J. W. *Biochem. J.*, **54**, 682, 1953.
[12] van Heyningen, R., Pirie, A., and Boag, J. W. *Ibid.*, **56**, 372, 1954.
[13] Pirie, A., van Heyningen, R., and Flanders, P. H. *Ibid.*, **61**, 341, 1955.
[14] Pirie, A. and Flanders, P. H. *Arch. Ophthal., Chicago*, **57**, 849, 1957.
[15] Pirie, A., Schmidt, G., and Waters, J. W. *Brit. J. Ophthal.*, **32**, 321, 1948.
[16] Bembridge, B. A., Crawford, G. N. C., and Pirie, A. *Ibid.*, **36**, 131, 1952.
[17] Matoltsy, A. G. *J. gen. Physiol.*, **36**, 29, 1952.
[18] Walls, G. L. 'The Vertebrate Eye'. Cranbrook Institute of Science Bulletin No. 19, 1942.
[19] Weitzel, G., Buddecke, E., Fretzdorff, A. M., Strecker, F. J., and Roester, U. *Hoppe-Seyl. Z.*, **299**, 193, 1955.
[20] Weitzel, G., Strecker, F. J., Roester, U., Buddecke, E., and Fretzdorff, A. M. *Ibid.*, **296**, 19, 1954.
[21] Sowden, E. and Pirie, A. (Unpublished.)
[22] Jakus, M. A. *Amer. J. Ophthal.*, **38**, 40, 1954.

Some recent advances in molecular biology

M. F. PERUTZ

Molecular biology seeks to explain biological function in terms of molecular structure. Great strides have recently been made, and it is now widely expected that the simplest forms of life will be understood in molecular terms within the next twenty years. The key problems are the structure of the nucleic acids, on which genetic replication and protein synthesis depend, and the structure of the protein catalysts which control metabolic activity. This article discusses the structure and function of nucleic acids. It describes the first three-dimensional model, obtained by X-ray analysis, of a protein molecule and tentative models of small viruses. It also shows how genetic mutations act by altering the constitution of protein molecules.

GENES AND ENZYMES

The bewildering variety of living forms conceals an underlying unity in the molecules that nature uses for the processes of reproduction, multiplication, growth, movement, metabolism, secretion, and nervous response. Similar enzyme molecules catalyse the same reactions in unicellular organisms and in mammals; some of the same co-factors are probably at work in glycolysis and in photosynthesis; the same few simple molecules are used in the biosynthesis of the many complex organic compounds found in living organisms. Almost all metabolic processes are catalysed by enzymes and all enzymes are protein molecules. By teaching this creed twenty-five years ago Sir Frederick Gowland Hopkins created the scientific climate in which our research on the chemical structure and spatial architecture of proteins was begun.

In recent years biochemists have started to probe deeper, asking themselves what controls the synthesis of enzymes. It cannot be other enzymes, since they would have to be made by yet more enzymes and so on *ad infinitum*. We now know that enzyme synthesis is controlled by genes and we have good reason to believe that one gene controls the synthesis of one enzyme. A gene must therefore possess a dual function; it must be able to replicate itself and to determine the specific structure of a protein molecule. This poses the question of the chemical nature of genes.

It would appear the simplest hypothesis, at any rate at first sight, to suppose that enzymes were self-reproducing molecules in addition to being functional catalysts. However, recent research on viruses and bacterial transforming factors has given convincing proof that the essential part of a gene is made not of protein, but of nucleic acid. This may be of two different kinds: deoxyribonucleic acid (DNA) in cellular organisms and large viruses, or ribonucleic acid (RNA) in certain small viruses. Biological replication and metabolic activity therefore appear to depend primarily on the structure and interaction of two types of very large molecules: nucleic acids and proteins. The part played by lipoids and polysaccharides is not yet clear; at present it seems to be secondary.

The basic questions that biologists have long been asking, therefore, are these. What is the structure of the genetic material? How does it replicate itself? How does it control the synthesis of enzymes? What structures do enzymes have, and how do the structures determine their catalytic function?

THE STRUCTURE AND REPLICATION OF THE GENETIC MATERIAL

We are used to thinking of enzymes as molecules, but the idea of the gene as a molecule with a definite stereochemical structure is relatively new. We think of genes in an abstract way as unit factors of heredity which are arranged in a linear order along the chromosomes, or perhaps the term gene conjures up a picture of the banded structures that can be seen in the giant chromosomes of the fruit fly. Chemically, chromosomes consist of DNA and protein; RNA occurs at some stages of the mitotic cycle, but since it is absent in sperm, it can safely be excluded as a prime carrier of hereditary information in higher organisms. The idea that it is the DNA alone that carries the genetic information gained validity with O. T. Avery's discovery of bacterial transforming factor and has become widely accepted only since A. D. Hershey and M. Chase demonstrated DNA to be the main infective component and the carrier of genetic information in bacterial viruses.

It might be argued that the hereditary apparatus of higher organisms need not necessarily be

the same as that of microorganisms. This may be true, and indeed there is as yet no direct proof of the part played by nucleic acid in the chromosomes of higher animals. However, the constancy of the DNA content and composition in all cells of a given species, its metabolic inertness, and a variety of other indirect evidence make us believe that DNA is in fact the sole carrier of genetic information in all organisms except the small viruses, where its place is taken by RNA. It is sometimes argued that an entirely new class of compound may yet be discovered that might revolutionize our ideas on this matter, but there is at present no experimental basis for this argument.

If the nucleic acids are to convey genetic information they must be so made as to form a chemical code. They are in fact long-chain polymers, with a backbone in which an identical chemical pattern repeats at regular intervals, forming the links of the chain (figure 1). Attached to each

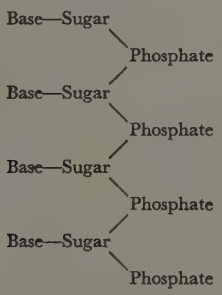


FIGURE 1 – *Chemical structure of DNA. The compound consisting of one phosphate, sugar, and base is called a nucleotide.*

link is a purine or pyrimidine base. In any one nucleic acid these bases are of four different kinds. We do not yet know in what sequence the bases are arranged in any nucleic acid, nor do we have any direct information that they are arranged in any definite sequence at all; we know only that their proportions are characteristic and constant in the DNA of any particular species. It is the fact that the bases are the only variable constituents that makes us believe that they are arranged in a definite sequence and that this sequence constitutes the genetic code. If this is true, then the genetic language is written in a four-letter alphabet on an immensely long scroll. The actual length of the scroll is about 0·003 mm in a small plant virus, 0·1 mm in T2 bacteriophage, and 1000 mm in a mammal, i.e. many times the length of the virus or cell that contains it. The number of nucleotide letters which these lengths correspond to are 8000, 500 000 and 3000 million respectively, the last equivalent to a great library of information.

Each time a parent cell divides, an exact copy of the genetic information has to be made in order to ensure continuity of inheritance in the daughter cells. We do not yet know how this is done, but J. D. Watson and F. H. C. Crick have proposed a structural model of DNA that suggests some features of a possible mechanism [1]. Their model is of special interest in this context because it shows most clearly how a new concept of molecular structure can give birth to new ideas of biological function, and may even eventually lead to the interpretation of pathological changes.

The Watson-Crick model of DNA consists of two chains that run in opposite directions and are coiled around each other to form a double helix (figure 2). It looks like a spiral staircase in which the bases form the steps and the phosphate ester chain provides the banisters. Each step consists of two bases, one from each of the chains, which are linked together by hydrogen bonds. Suppose now the four different types of bases which form the letters of the genetic alphabet are called A, T, G, and C, then the model predicts that only specific pairs of bases can be linked to form a step,

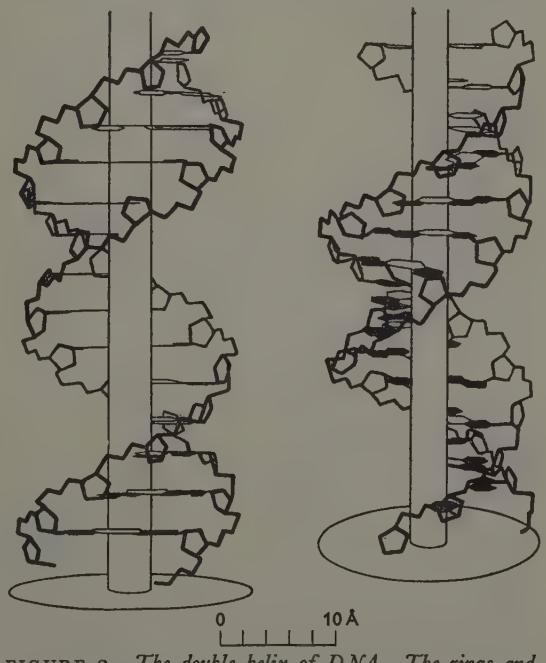


FIGURE 2 – *The double helix of DNA. The rings and wire links signify the phosphate ester chain. The plates between them represent the bases. (Reproduced by permission from F. H. C. Crick and J. D. Watson,* Proc. roy. Soc., A, 223, 80, 1954.)

such that A is always linked to T and G to C. This implies that the sequence of bases in the two chains making up the double helix must be complementary, so that the sequence on one chain determines that on the other (figure 3).

When we want to copy a document we prepare a negative from which we make a positive print. The complementary sequence of bases in the two chains makes DNA a duplex of positive and negative. To reproduce itself, the two components would have to separate and each would have to make a print of itself. In this way two copies would be formed, each carrying information identical to that of the parent duplex (figure 4).

By focusing people's ideas on a definite structure and a mechanism of replication, the Watson-Crick model has acted as a stimulus for a variety of interesting experiments. The model owed part of its inspiration to the X-ray diffraction work of M. H. F. Wilkins and R. Franklin [2]. These two workers and their associates have since proved that the X-ray diffraction patterns of DNA fibres, from whatever source, are fully consistent with the double helix of Watson and Crick, though certain features of the initial model need modification. Wilkins also proved the double helix to be present, not only in purified DNA fibres, but in live sperm heads, possibly with a third chain, of protamine, wound around it. We can be fairly sure, therefore, that the structure is right and that it occurs in live chromosomes.

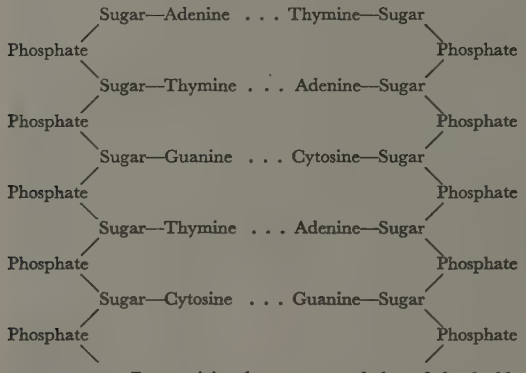


FIGURE 3 – *Base pairing between two chains of the double helix of DNA.*

An essential feature of the DNA code is its linearity. This prediction has been tested by S. Benzer, at Purdue University, in a most ingenious experiment on the genetic recombination of bacteriophage. The results of his work have shown that mutations can take place at as many as a hundred different sites within a single physiological gene, which can therefore no longer be regarded as an indivisible unit (figure 5). Moreover, Benzer was able to prove that all these mutating sites lie in a unique linear array, and that the distance between the most closely spaced loci can be no more than a few links in the nucleotide chain [3]. Thus, in one organism, the linearity of the genetic code on a molecular scale has now been verified experimentally.

We now come to the mechanism of replication.

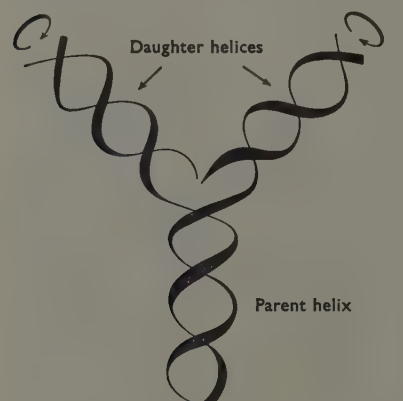


FIGURE 4 – *The scheme of Watson and Crick for the self-replication of DNA. Unwinding of the parent duplex, and replication, and rewinding of the duplicates would proceed simultaneously. All three arms of the* Y *would rotate as indicated. (After M. Delbrück and G. S. Stent, by courtesy of the Johns Hopkins Press.)*

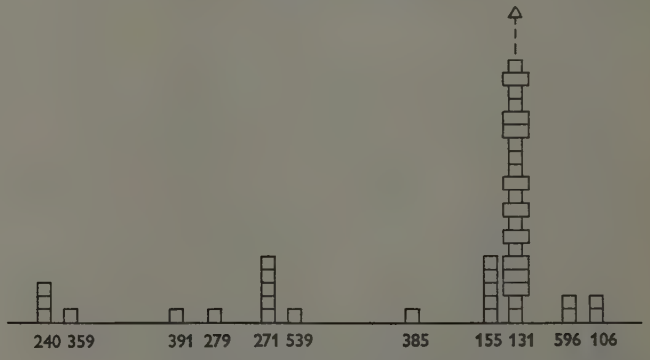


FIGURE 5 – *Genetic map of mutants along one short segment of one of the genes in T4 bacteriophage. Each box signifies one occurrence of the mutant. The distances between the mutants are based on recombination frequencies between them and have no direct meaning in physical terms, but rough calculations indicate that the physical distance between the most closely spaced mutants corresponds to a few links along a DNA chain. (After S. Benzer, by courtesy of the Johns Hopkins Press.)*

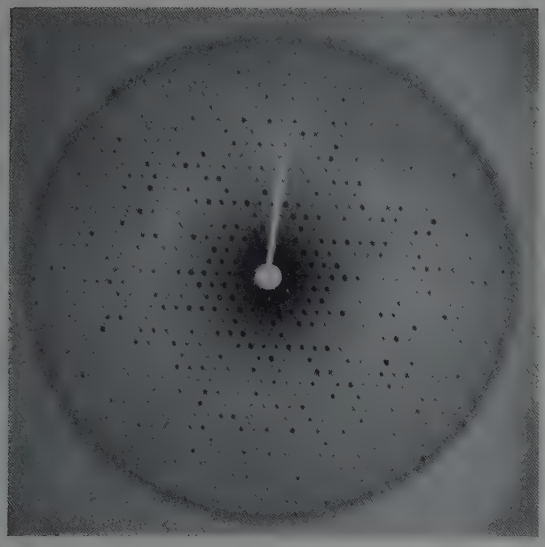


FIGURE 6 – *X-ray diffraction photograph from a single crystal of haemoglobin. Each spot is a diffracted image of the crystal. The different intensities of the spots provide the information from which the structure is ultimately deduced.*

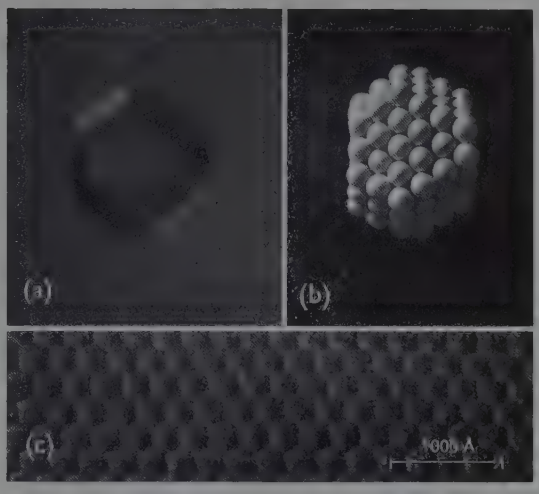


FIGURE 8 – (a) *Photomicrograph of crystal of poliomyelitis virus (Mahoney strain).* (b) *Ball model showing probable arrangement of virus particle.* (c) *Electron micrograph of virus particles regularly packed on one of the crystal faces. (Reproduced by permission from R. L. Steere and F. L. Schaffer,* Biochem. Biophys. Acta, **28**, 241, 1958.)

Watson and Crick's model suggests that in each cycle of replication one of the two parent strands of the double helix should go to each of the new double helices (figure 7). This prediction can be tested by labelling the parent DNA with isotopes and then determining the distribution of the labels in the DNA of the progeny. Several ingenious experiments of this type have now been done; one on bacteriophage, one on *E. coli*, and the third on the chromosomes of bean seedlings. Each has given an answer consistent with the mechanism of replication indicated in figure 7, though two of the experiments leave some doubt whether the transferred label is really part of the DNA that carried the genetic code.

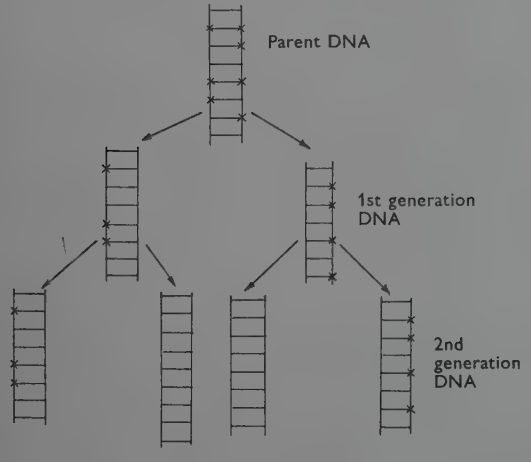


FIGURE 7 – *Distribution of isotopic label of parent DNA among double helices of progeny DNA. The crosses indicate isotopic markers.*

On the chemical side, a cell-free enzyme system has been isolated from *E. coli* which synthesizes DNA, provided all four bases are present among the nucleotide precursors. A further condition for synthesis is the presence of a primer, and this primer has to be DNA. These conditions are in accordance with expectation if synthesis of a DNA chain requires the presence of a complementary chain on which it can grow, like a bindweed, and if growth would be interrupted if one of the four bases necessary for pairing were absent.

It would be too early to say that the mechanism of genetic replication suggested by the Watson-Crick model has been proved conclusively, but supporting evidence is steadily accumulating. On the other hand, there are still two important aspects of replication which are far from clear, and which any general theory ought to be able to explain. One is the origin of mutations and the other is the mechanism of crossing over. The model suggests that the simplest mutation should consist in a replacement of one base pair in the DNA chain by another, say A–T by G–C; the action of certain chemical mutagens is indeed consistent with this idea. However, there is the

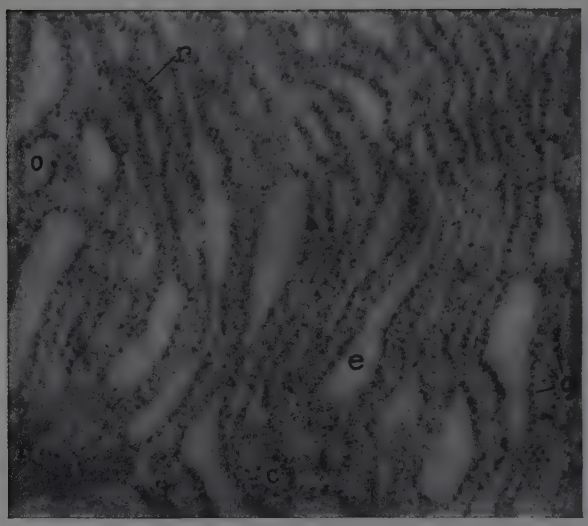


FIGURE 9 – *Electron micrograph of thin sections through a rat pancreas. The field is taken up by structures known as endoplasmic reticulum (e, c, and o) whose matrix contains many small dense granules (g and r). These are the microsomal particles which synthesize proteins. (Reproduced by permission from G. E. Pallade,* J. Biophys. Biochem. Cytol., 1, 68, 1955.)

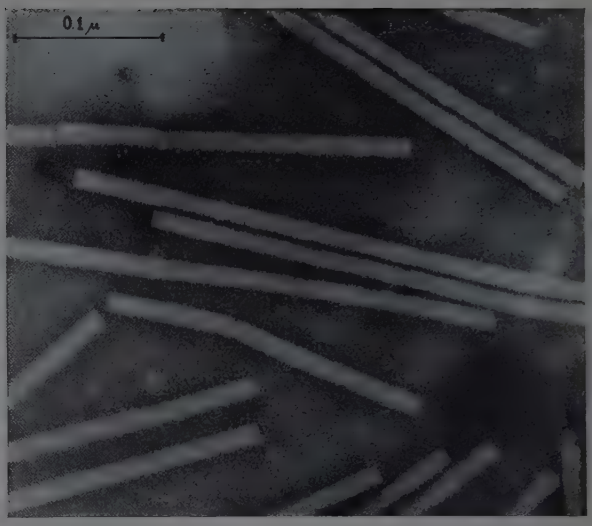


FIGURE 10 – *Rods of tobacco mosaic virus stained with phosphotungstic acid which fills the central hole and shows it up as a dark line.* (0·1 μ = 1000 Å.) (*S. Brenner and R. Horne.*)

further prediction that the probability of such a replacement occurring should be the same anywhere along the chain. This is not borne out by Benzer's results, which indicate the frequency of mutation to be unequal at different genetic sites.

So far as I know, no plausible working hypothesis has yet been produced for a molecular mechanism of crossing over. Nevertheless, the multitude of interesting experiments now being carried out on the replication of bacteriophage, on the transformation and transduction[1] of bacteria, and on the genetics of many kinds of microorganisms are steadily adding to our understanding of genetic events. It is not too rash to predict that the structure and replication of the genetic material may be understood in as much detail in ten years' time as, for instance, the biosynthesis of fatty acids is today. Analysis of the processes in the mitotic cycle of multicellular organisms may follow the fundamental research on the molecular structure of cell constituents and should not be regarded as beyond our reach.

[1] Transformation is a genetic change in one strain of bacteria induced by the transfer of the DNA extracted from another strain. Transduction is the transfer of genetic characters from one strain of bacteria to another through infection by lysogenic phages.

In this account I have left on one side the structure of RNA because it is still unknown and because it acts as a carrier of genetic information in only the small viruses. However, as will be seen in the following section, it is RNA and not DNA that directly controls protein synthesis; RNA may also act as a carrier of genetic information from the nucleus to the cytoplasm, and its structure is therefore of supreme interest. Unfortunately, fibres of RNA have so far given too poor an X-ray diffraction pattern to serve as a basis for a structural model. The problem is therefore being studied indirectly. S. Ochoa has isolated an enzyme which synthesizes RNA-like fibres of variable composition from simple precursors. A. Rich has shown that many synthetic analogues give better X-ray pictures than natural RNA and provide valuable information about the kinds of structures which RNA might form under various conditions, such as double and triple helices. It looks as though the solution of the RNA structure is not too far distant [4].

STRUCTURAL ASPECTS OF PROTEIN SYNTHESIS

Having discussed the structure and replication of the genetic material, we can now consider its

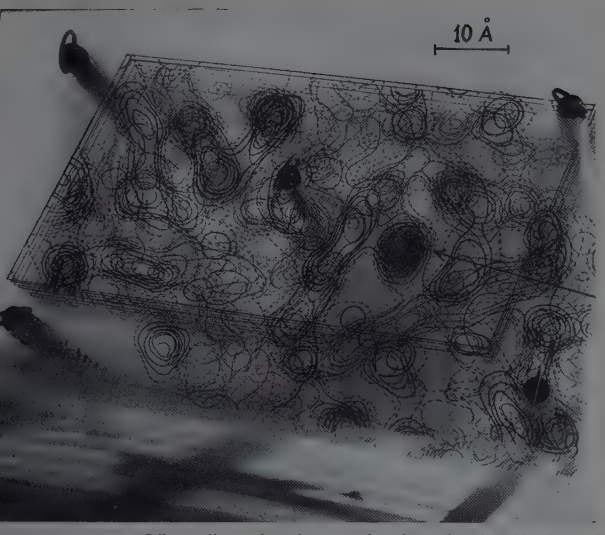


FIGURE 11 – *Three-dimensional map showing the distribution of density along a series of parallel sections through two neighbouring molecules in a crystal of myoglobin. The arrow points at the high peak representing the iron-containing haem group. (After J. C. Kendrew.)*

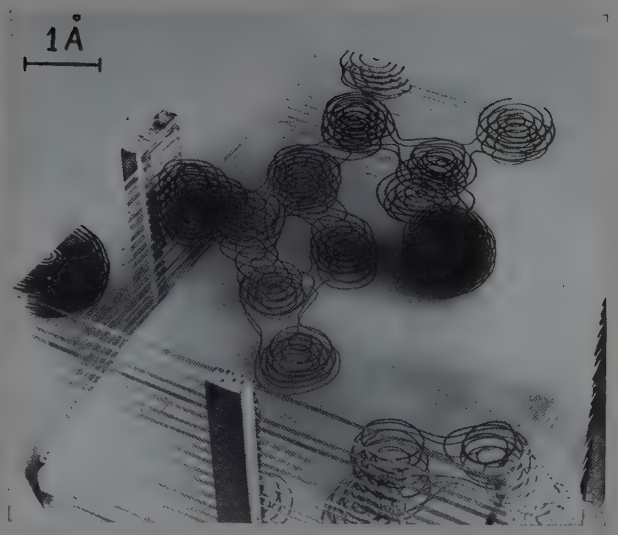


FIGURE 12 – *Sections through penicillin molecules, in which the atoms show up as peaks of high electron density. Note the difference in scale between figures* 11 *and* 12. *(After D. Crowfoot* et al, *by courtesy of the Princeton University Press.)*

function. If a gene determines the specific structure of an enzyme, then the meaning of the genetic code would be expressed in terms of protein structure. This question can be treated in a purely formal manner, regardless of the actual chemical mechanism involved in protein synthesis.

Consider the structure of a protein in relation to that of a nucleic acid. The unique feature that the two substances have in common is a specific linear sequence of different units on a long chain. What distinguishes them is the number of different kinds of unit which each contains. Any one nucleic acid contains mainly four different kinds of bases, whereas proteins contain mainly twenty different kinds of amino acids, and it is the sequence of these which determines their specificity. We now assume as a working hypothesis that the sequence of the four bases along the nucleic acid chain determines the sequence of amino acids along the protein chain, and that this is the real purpose of the genetic code.

These formal ideas suggest that the actual apparatus for synthesizing proteins is a nucleic acid template on which the amino acids are assembled in the right order before they are linked together to form a polypeptide chain. From what has been said so far, one would naturally expect these templates to occur in the cell nucleus and it is surprising that the rate of protein synthesis in the nucleus is low. Nevertheless, most protein is probably made in the cytoplasm, where the point of polymerization seems to have been tracked down to small spherical particles which have been named microsomal particles (figure 9). They have molecular weights of the order of a few millions and consist of only RNA and protein. There is evidence that it is the RNA in these particles which forms the templates on which protein chains are made [5].

It will now be apparent why it is so important to solve the structure of RNA. We hope that knowing the structure of the RNA template will help us to guess the mechanism by which the amino acids are assembled and joined. Great strides have been made in the last few years in elucidating the chemical mechanism by which amino acids are activated and brought to the assembly line.

M. Hoagland and others have discovered activating enzymes that join amino acids to adenosine monophosphate (AMP). Hoagland has also shown that these activated amino-acid-AMP-anhydrides are probably attached to soluble RNA of relatively small molecular weight as a carrier system before entering the microsomal particles [6]. It now looks as though the cytoplasm

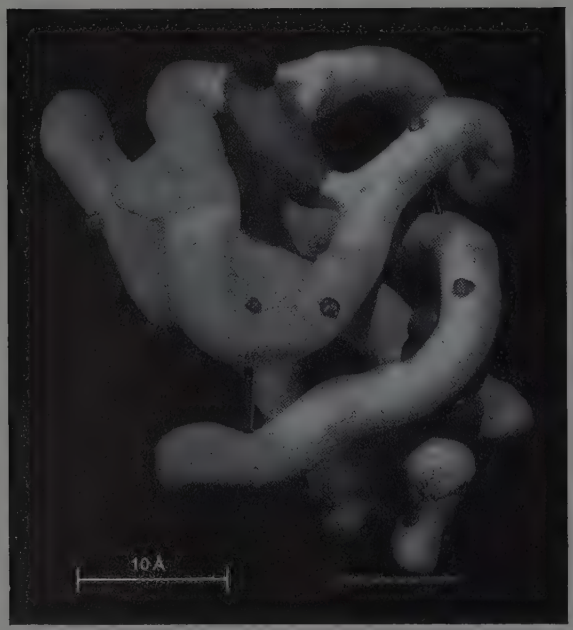


FIGURE 13a – *Model of the myoglobin molecule. The white sausage represents the polypeptide chain; the grey disk is the haem group. The little balls represent the positions of different heavy atoms used for determining the structure. The scale is in Ångström units.*

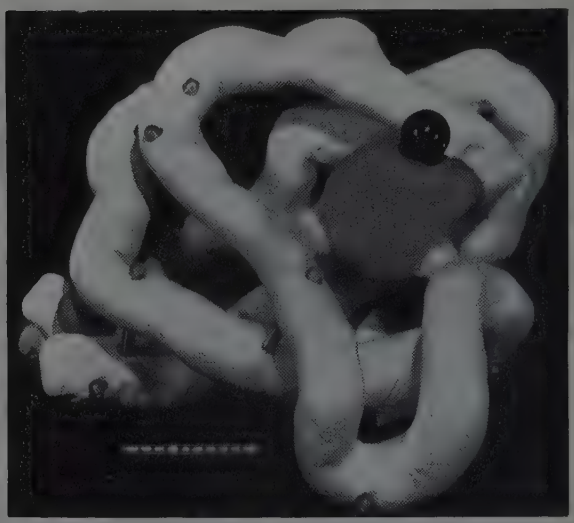


FIGURE 13b – *Top view of the molecule shown in figure* 13a [10].

FIGURE 14 – *Model of symmetrical packing of* 60 *identical sub-units on the surface of a sphere (F. H. C. Crick). This might represent the structure of the protein shell of certain plant viruses or perhaps of poliomyelitis virus. The RNA is not shown.*

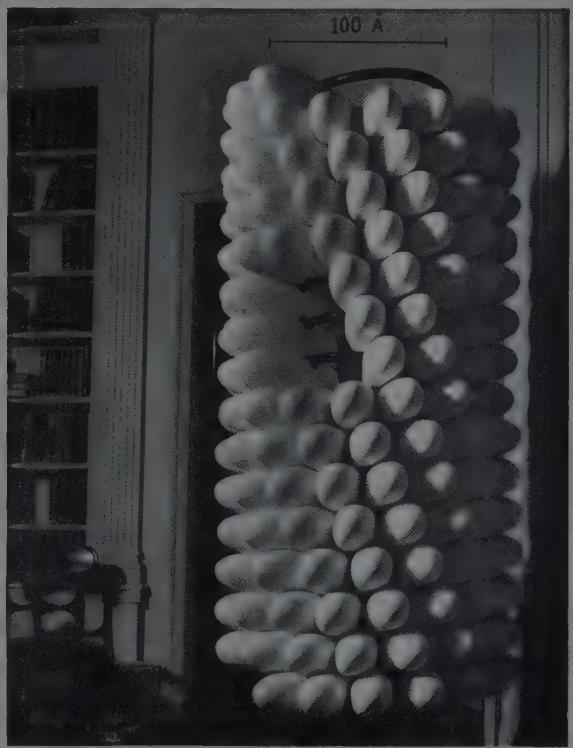


FIGURE 15 – *Model of tobacco mosaic virus. Each 'loaf' represents a protein sub-unit of molecular weight* 17 000. *The opening shows the coils of RNA inside the particle. The pitch of the coil is* 23 *Å. (Rosalind Franklin and A. Klug.)*

contains at least two different kinds of RNA, one having a metabolic function and the other serving as a template for protein synthesis. The time may not be far off when a fusion of chemical and structural ideas will lead to the discovery of the synthetic mechanism. On the other hand, we do not yet know how the genetic information is transferred from the DNA in the nucleus to the RNA in the cytoplasm, and this is one of the important questions for the future.

STRUCTURE OF PROTEINS

Like the nucleic acids, the proteins are giant molecules. They consist of polypeptide chains in which the same chemical groups

—CO—RCH—NH—CO—RCH—NH—

repeat at regular intervals. Specificity is provided by the side-chains (R) of the twenty different kinds of amino acids (figure 16).

An enzyme molecule may consist of one or more such polypeptide chains which, together, may contain between a hundred and several thousand amino acid residues, all arranged in a definite sequence. The number of chains and the sequence of residues within them constitute the primary structure of a protein.

As in nucleic acids, the secondary bonds of the various groups in a polypeptide chain can be best satisfied if the chain is coiled into a helix. The α-helix of Pauling and Corey (figure 17) is the most stable, but not the only, kind of helical configuration that the chain can assume. The kind of helix formed or, more generally, the way one residue is related to its neighbours along the chain, constitutes the secondary structure of a protein.

From what has been written so far the reader might conclude that protein molecules are thin threads or ropes. Collagen, hair, and some muscle proteins, for example, do indeed have a structure of this kind, but the majority of enzymes are probably spheroidal in shape. We must infer that the chains or helices in them are somehow folded backwards and forwards so that the complete molecule behaves in solution like a ball. This kind of folding constitutes the tertiary structure of a protein.

Many enzymes contain one or more non-protein (prosthetic) groups that form the site of their catalytic activity. Their exact function generally depends on combination with a specific protein.

To complete this introduction to protein structure one further important point should be made. Not only is the number of polypeptide chains and sequence of amino-acid residues in a protein definite and specific, but the same is true of its secondary and tertiary structure. In fact, a protein molecule is like an animal in having a

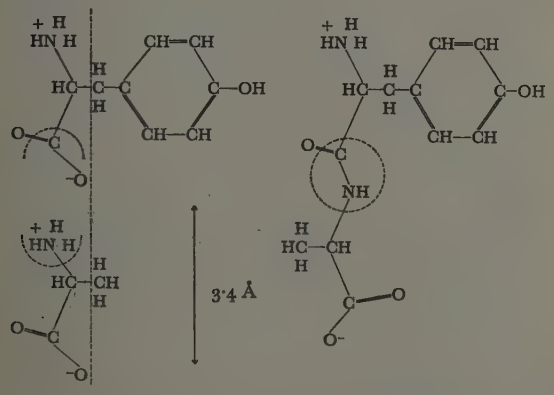


FIGURE 16 – (*left*) *Two amino acids, tyrosine above and alanine below. The part to the left of the broken line is the same in all amino acids and is incorporated in the main chain. The groups on the right form the different side-chains.* (*right*) *The two amino acids joined by a peptide bond. This leaves free the amino group at the top and the carboxyl group at the bottom to form peptide links with further amino acids until a long chain is formed.*

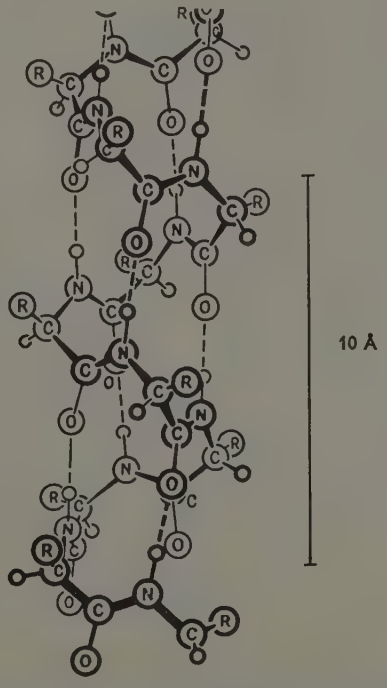


FIGURE 17 – *The α-helix of Pauling and Corey. The atoms marked R represent side-chains.* (*By courtesy of L. Pauling, R. B. Corey, and H. R. Branson,* Proc. Nat. Acad. Sci. Wash., 37, 207, 1951.)

three-dimensional anatomy laid out to a definite plan, rigid in some parts and flexible in others, with perhaps some minor variations in different individuals of the same species.

By chemical and kinetic studies a great deal has been discovered about the catalytic site of certain enzymes, and the nature of the reactions they catalyse, but no detailed knowledge yet exists about the structure of any enzyme and not even the most rudimentary information about the great majority of them. The problem really requires a twofold approach: a chemical one, to find the number of chains, the sequence of residues, and the nature of the bond between protein and prosthetic group; and a physical one to discover the way the polypeptide chains are coiled and folded and the nature of the secondary chemical bonds which hold them together. Both approaches have been developed by members of the Medical Research Council's staff at Cambridge, one at the Department of Biochemistry by F. Sanger and his colleagues and the other by the Molecular Biology Unit at the Cavendish Laboratory. Both methods are laborious in the extreme.

Sanger's chemical approach reached its climax with his determination of the constitution of insulin, which contains 51 residues arranged in two closely linked chains (figure 18) [7]. His discovery was one of the milestones in protein chemistry. First of all it removed the last shadow of doubt from the polypeptide hypothesis which Hofmeister had enunciated more than fifty years earlier. It established the fact that the amino-acid residues really are arranged in a definite, genetically determined sequence, but disproved the widely held belief that this sequence was regular. It revealed the part played by cystine bridges in the architecture of protein molecules, and the chemical nature of species specificity. Most important of all, Sanger demonstrated that the complete formula of a protein can be determined by chemical methods, at least as far as the primary covalent bonds are concerned, and thereby stimulated a great volume of new research all over the world.

Since Sanger completed this work two years ago, he and others have tried to improve the methods of sequence study and to apply them to larger proteins, but the difficulties of fractionation and analysis rise rapidly with the size of the protein and each analysis of even a small protein is expected to take a team of research workers several years. On the other hand, the number of known enzymes is over 500 and most of them have molecular weights many times larger than insulin, which shows that the development of more rapid and sensitive methods is vitally important.

The physical approach to the structure of crystalline proteins is based on X-ray analysis. It involves studies of the X-ray diffraction patterns, generally from single crystals, and is a technique that has been widely used to determine the atomic arrangement in organic compounds. Most of these compounds, however, were at least a hundred times smaller than protein molecules, and it was a matter of great difficulty to extend the methods of X-ray analysis to molecules of such enormous size [8]. None of the approaches yielded much information until the writer discovered, in 1953, that the problem could be solved by studying the X-ray diffraction pattern from an isomorphous pair of crystals, one containing the protein alone and the other a complex of the protein with a heavy atom such as mercury. Soon afterwards it became apparent that one isomorphous pair would not be enough and that a whole series of isomorphous heavy atom compounds would be needed, each compound having a heavy atom attached to a different site on the protein molecule [9]. This method has now become the basis for the structure analysis of crystalline proteins and viruses in many laboratories (figure 6).

The greatest success of the method has been achieved during the past few months, when J. C. Kendrew was able to build the first three-dimensional model of a protein molecule ever to be made. It represents myoglobin, a protein of molecular weight 17 000 consisting of one long polypeptide chain with 153 residues in unknown sequence, plus one haem molecule, the same as in haemoglobin, as a single prosthetic group. Like

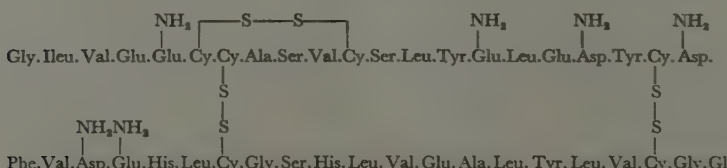


FIGURE 18 – *The chemical constitution of beef insulin. Gly.* = *glycine; Ileu.* = isoleucine; *Val.* = *valine; etc.* (*Reproduced by permission from A. P. Ryle, F. Sanger, L. F. Smith, and R. Kitai* [7].)

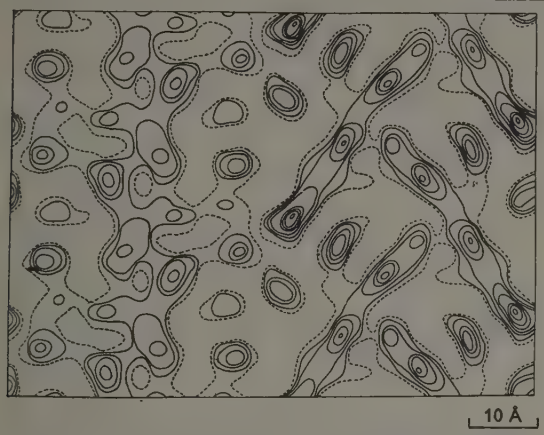


FIGURE 19 – *Section through several myoglobin molecules. The long ridges of high density on the right represent polypeptide chains* [10].

haemoglobin, myoglobin combines reversibly with molecular oxygen; it is used by vertebrates to store oxygen in muscle.

Kendrew's model is the result of a three-dimensional X-ray analysis which shows the distribution of density in the myoglobin molecule along a series of parallel sections, rather like a series of microtome sections of a tissue, but on a thousand times smaller scale (figure 11) [10]. Figure 19 is an example of one such section which takes the form of a contour map with the hills and valleys signifying regions of high and low density. Usually sections of this kind, obtained by X-ray analysis, can resolve individual atoms, like the ones of penicillin shown in figure 12, but when analysing molecules as large as proteins, it is convenient to approach atomic resolution by stages. At this first stage of the three-dimensional analysis of myoglobin the resolution is only 6 Å, which is too coarse to resolve individual amino-acid side-chains, let alone atoms, but sufficient to show the haem group and large parts of the polypeptide chain. The chain, at this resolution, is a cloud of high density, like the vapour trail of an aeroplane, without much differentiation; the haem group, with its central iron atom recognizable by its high density, resembles a slightly squashed sphere. By tracing the course of the regions of high density through the different sections, Kendrew was able to build a plausible model of the myoglobin molecule (figure 13). This reveals a remarkably intricate structure, much more complex than anything we had imagined. The polypeptide chain is folded and turned in a complicated three-dimensional basketwork and enmeshes the haem group in a subtle manner. From one of the density sections it is possible to infer the point of attachment of the iron atom to the polypeptide chain, but in addition there seem to be at least two other points of contact between the chain and the protoporphyrin ring. Only the side on which the oxygen attaches itself is left clear. The nature of the chemical groups involved in the interaction between the haem group and the polypeptide chain cannot yet be resolved, and neither can the configuration of the chain itself, but from the distance between different portions of the chain in regions where it folds back on itself, and from its cylindrical shape, one would guess that it is coiled into a helix. What kind of helix is not yet clear.

Kendrew, at the next stage of his analysis, will try to raise the resolution to 2 Å, which should suffice to show up the turns of the helix and the positions of the larger side chains. Atomic resolution is still far off and fraught with difficulties.

The writer's own work is concerned with the structure of haemoglobin, which has a molecular weight of 67 000, four times larger than myoglobin, and contains four polypeptide chains and four haem groups. It consists of two identical halves (not four identical quarters) which are joined together to form a roughly spheroidal molecule with the dimensions $55 \times 55 \times 70$ Å. While the model of myoglobin is based on an analysis of the density distribution along a series of closely

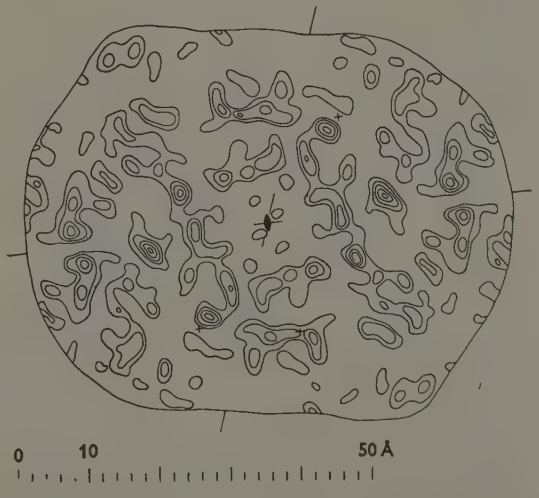


FIGURE 20 – *Picture of the density distribution in the haemoglobin molecule, seen in projection on a plane. The symbol at the centre represents an axis of two-fold symmetry which requires that the molecule consists of two structurally identical halves. Peaks represent regions of high density. Contours in the valleys are omitted.*

spaced sections through the molecule, all we can show of haemoglobin at present is the density distribution seen in projection on a plane (figure 20). This figure has a resolution of 2·8 Å, in principle sufficient to distinguish significant detail, but suffers from the overlapping of the many features that are all projected on the same plane, rather like the X-ray picture of an animal in which all the different organs appear superimposed. This projection, however, is merely a stage in the development of the three-dimensional analysis, which should lead to a molecular model in the not too distant future. We hope that this will show the arrangement of the four haem groups and of two out of the six sulphydryl groups, and the general layout of the four polypeptide chains. With luck we might also be able to see how the two halves of the molecule are joined together and the relation between the structures of myoglobin and haemoglobin [11].

The reader may well ask what purpose is served by these elaborate analyses. Supposing a good fairy appeared in the night and left us a folder giving the positions of all 10 000 atoms in the haemoglobin molecule, what good would it do us? Sanger's analysis of insulin has taught us what kind of primary structure to expect in proteins, but before Kendrew's myoglobin model nothing was definitely known about their secondary or tertiary structure. The complete solution of a protein structure by X-rays would open a mine of stereochemical information and would furnish rational explanations for the basic phenomena of protein chemistry, such as enzymatic activity, denaturation, solubility, accessibility of chemical groups, and species specificity. Probably some architectural principles applying to proteins generally would also emerge, but at this stage one cannot be sure if such principles exist or if they would be overshadowed by the specific individuality of each particular protein. Detailed understanding of protein structure is crucial for biology and medicine and may ultimately lead to a far deeper understanding of physiological and pathological functions.

In addition to these wider aims, which apply to the X-ray study of any crystalline protein, there are specific reasons for concentrating on the structure of oxygen carriers. The attraction is the unique and central position which iron-porphyrin complexes take up in cellular and animal metabolism. Haem by itself does not form a compound with molecular oxygen; this property is conferred upon it by the combination with the specific protein globin. We want to determine the nature of the bonds that hold haem and globin together.

The difference between the oxygen-combining properties of myoglobin and haemoglobin needs consideration. The former has a hyperbolic dissociation curve, while the latter exhibits a characteristic sigmoid curve. This happens because myoglobin has only one haem group, so that its reaction with oxygen follows a unimolecular law, while in haemoglobin the four haem groups influence each other's affinity for oxygen. Moreover, the haemoglobin molecule as a whole undergoes a distinct structural change on oxygenation and reduction, while myoglobin does not. Knowledge of the positions of the four haem groups, and of any possible change in those positions during oxygenation and reduction, can be obtained only by X-ray analysis. It would perhaps help us to understand the two most important physiological properties of haemoglobin: the sigmoid oxygen dissociation curve and the Bohr effect, that is the fact that oxyhaemoglobin is a stronger acid than reduced haemoglobin, and therefore absorbs less carbon dioxide. The structural differences between adult and foetal haemoglobin would be another important problem to solve.

That the iron-combining property is specific to the combination of haem with globin has already been stressed. Other, quite different, chemical reactivities are conferred upon the same haem group if it is combined with different proteins. In haemoglobin the iron atoms remain in the ferrous state throughout oxygenation and reduction. In the cytochromes which act as respiratory enzymes, catalysis involves rapid oxidation and reduction between the ferrous and ferric states. The peroxidases and catalases, by contrast, are normally in the ferric state and serve as catalysts for the oxidation of certain reducing agents by peroxides and some other strong oxidizing compounds. The molecular weight of catalase (224 000) is too large for crystallographic study, but peroxidase (41 000) and cytochrome C (13 000) lie within the possible range. Cytochrome C has been crystallized for the first time and examined by X-rays in a preliminary way by G. Bodo [12].

At present oxygen carriers and respiratory enzymes in which the site of the catalytic activity is known probably offer a more promising field for X-ray analysis than, say, proteolytic enzymes which contain no prosthetic group. It may, however, become possible to learn something about the catalytic sites of other enzymes by studying crystalline complexes of enzyme and inhibitor.

So far this account of protein structure has been restricted almost exclusively to soluble proteins, and little has been said about the fibrous ones whose main function is contractility, protection, and structural support. Pauling and Corey's α-helix and pleated sheet, and the triple helix recently proposed by several groups of workers for collagen, have established the general principles on which fibrous proteins are built. A major unsolved problem left now is the detailed structure of the two muscle proteins, myosin and actin, and its relation to the sliding mechanism of muscular contraction recently discovered by H. E. Huxley and A. Hanson, and by A. F. Huxley and F. Niedergerke. This is a large problem of its own which belongs to quite a separate field of molecular biology, the field of structure and movement, which has been discussed by H. E. Huxley in a recent article in ENDEAVOUR [13].

PROTEIN STRUCTURE, MUTATIONS, AND SPECIES SPECIFICITY: STRUCTURE OF ANTIBODIES

Having discussed the structure of nucleic acids and proteins, we might consider once more the relation between a gene and its product by examining the effect of genetic mutations on proteins. If there really exists a direct correspondence between the sequence of base pairs in DNA and the sequence of amino-acid residues in a polypeptide chain, then a mutation, consisting in a change of the genetic code, should express itself in a change of amino-acid sequence.

Let us begin by considering the effect of a single mutation. Sickle cell anaemia and haemoglobin C disease are two congenital defects which are inherited in a Mendelian manner. Each is due to the appearance of an abnormal haemoglobin which harmfully alters the properties of the red cell. During the last year V. M. Ingram and J. A. Hunt have discovered that the abnormality consists in the change of a single one out of about 300 amino-acid residues in the haemoglobin half-molecule, one particular glutamic acid residue being replaced by valine in sickle cell haemoglobin and by lysine in haemoglobin C (figure 21) [14]. Looked at from the point of view of protein chemistry, this discovery shows us that the alteration of a single residue sensitively placed in a protein molecule may have a profound effect on its physiological properties. Genetically, the fact that the change is the smallest possible suggests that it is due to a single mutation in the haemoglobin gene, and the observation that it is the same residue which is replaced in the two different abnormalities suggests that, on the molecular scale, the position of the sickle cell mutation is very closely linked, if not identical, with the position of the haemoglobin C mutation.

Hb A . . . $\overset{+}{\text{His}}$—Val—Leu—Leu—Thr—Pro—*Glu*—$\overset{-}{\text{Glu}}$—$\overset{+}{\text{Lys}}$ . . .

Hb S . . . $\overset{+}{\text{His}}$—Val—Leu—Leu—Thr—Pro—*Val*—$\overset{-}{\text{Glu}}$—$\overset{+}{\text{Lys}}$ . . .

Hb C . . . $\overset{+}{\text{His}}$—Val—Leu—Leu—Thr—Pro—*Lys*—$\overset{+}{\text{Glu}}$—$\overset{+}{\text{Lys}}$ . . .

FIGURE 21 – *Sequence of amino-acid residues in a small segment of one of the polypeptide chains in haemoglobin. The three rows show the sequence in normal human haemoglobin (Hb A), in sickle cell anaemia haemoglobin (Hb S), and in haemoglobin C disease (Hb C). It is seen that all the residues except one (in italics) remain unaltered.*

Ingram's discovery has demonstrated most clearly and strikingly that mutations work on a very fine scale, but the same is really evident from the way evolutionary changes manifest themselves in the structure of proteins. It is well known that the amino-acid composition, crystalline form, antigenic character, and other properties of a given protein vary from species to species. Recent work by F. Sanger, V. Du Vigneaud, C. H. Li, and others has given us an insight into the alterations in amino-acid sequence which such differences between the species imply. Sanger and his colleagues found, for instance, that the great bulk of the insulin molecule remains unaltered in species as widely separate as cattle, horse, pig, sheep and whale. Replacements occur in only one 'species-sensitive' region which lies between the two halves of the cystine residue forming the internal bridge in one of the two chains. One alanine is liable to be exchanged for a threonine, one glycine for a serine, and one valine for an *iso*leucine [15]. These changes are evidently harmless, though the cystine bridge, to which the variable residues are attached, is known to be essential for hormone activity. It is not clear whether these particular three residues are variable because they correspond to an unstable region of the insulin gene or because mutations leading to the replacement of any of the other 48 residues in the insulin molecule would be lethal. Species differences consisting in the replacement of one or two residues in a long chain have also been found in other hormones.

The variations in these peptides and proteins give expression to some of the mutations by which the species have evolved. What impresses us most about them is that mutations appear to work on so fine a scale as to affect only one residue at a time. Many of us believe, though we would find

it hard to justify our belief, that the cause of such mutations is the replacement of a single base pair in the double helix of DNA which constitutes the gene. Even if this belief cannot be verified yet, it should at least be possible to test the sequence hypothesis indirectly by correlating genetic data on the sequence and spacing of mutating loci within a gene with chemical data on the variations in amino-acid sequence controlled by that gene. Benzer's bacteriophage system, in which he was able to map over a hundred loci within a single gene, offers a possible opening for such work.

One other problem which might be re-examined in this context is the structure of antibodies. The question concerns the difference between two antibody molecules made in response to two different haptens. Does it merely lie in a different folding of the polypeptide chain in two chemically identical proteins, or is it due to an alteration in amino acid sequence? The extremely sensitive methods of analysis now being developed by Sanger and by Ingram might furnish an answer to this question.

STRUCTURE OF SMALL VIRUSES AND MICROSOMAL PARTICLES

While bacteriophage has been the virus of choice for studies of genetics and growth, the small plant viruses have proved excellent material for research on molecular structure. Unlike bacteriophage and other large viruses, these contain only RNA and no DNA. The RNA is combined with proteins in proportions which vary widely in different viruses. In the nineteen-thirties, when the plant viruses were first crystallized, someone called them 'naked genes', because they seemed to be self-reproducing molecules. Today we know that this was a misnomer. The beautiful work of H. Fraenkel-Conrat in Berkeley and of G. Schramm and A. Gierer in Tübingen has shown that the RNA alone is infective and carries genetic information. Thus the RNA of the virus is the gene, and we know now that it is not naked, but well wrapped up in a protein coat.

X-ray studies of viruses, like those of smaller crystalline proteins, were begun by J. D. Bernal about twenty years ago. In view of the truly gigantic size of the molecules and the great technical and theoretical difficulties involved, the results so far achieved, especially with the mosaic virus of the tobacco plant, are most impressive. Tobacco mosaic virus (TMV) has a molecular weight of 45 millions and consists of 5 per cent RNA and 95 per cent protein. It has the shape of a rod with a length of 3000 Å and a width of 170 Å, when wet (figure 10). What is remarkable about this rod is its crystalline character. X-ray pictures show that it contains a molecular pattern repeating at regular intervals along its length, which implies that the protein part of the virus, at least, must consist of a regular array of identical sub-units.

In the course of the last five years a combination of independent X-ray studies by J. D. Watson, D. Caspar, Rosalind Franklin, and A. Klug, and electron microscope observations by R. Williams, R. Hart, and H. E. Huxley, have given us an intriguing picture of the internal structure of TMV (figure 15). Our first surprise was to discover that the rod is hollow, having a hole of 40 Å diameter running down its centre. Wound around this hole is a single long chain of RNA containing about 8000 nucleotides. We know nothing as yet about the geometry of this chain, but from the fact that it is at least ten times longer than the entire virus we can infer that it probably forms a helical coil, like the tungsten filament in an electric lamp. Enveloping the RNA coil is a helical array of protein molecules, as shown in figure 15. This much has been discovered by physical studies [16].

Chemical studies go further in telling us about the constitution of these protein molecules. They show that each has a molecular weight of 17 000 and probably consists of a single chain of 150 residues. The terminal residues at each end of the chain have already been determined, but the rest of the sequence is still unknown.

Several other rod-shaped plant viruses have been discovered with a structure closely related to TMV. The other small viruses look spherical under the electron microscope, and most of those that have been crystallized seem to be cubic, including poliomyelitis virus (figure 8). The structure of these spherical viruses is of great biochemical and medical interest. Their X-ray analysis shows how crystallographic symmetry can sometimes simplify a problem of apparently hopeless complexity, because in this particular instance the cubic symmetry of the crystals implies that the virus particles themselves consist of a certain number of symmetrically arranged sub-units of identical structure.

R. Markham suggested several years ago that turnip yellow virus consists of a shell of protein enclosing a core of RNA. His idea and the cubic symmetry led J. D. Watson and F. H. C. Crick to investigate how many different kinds of regular arrangements of circles can be drawn on the surface of a sphere. They soon found that this

problem had already been solved by Plato. Omitting arrangements that are inapplicable to asymmetrical molecules, the only possible numbers of circles are 12, 24, and 60, each having a different symmetry recognizable by its X-ray diffraction pattern. When seen under the electron microscope at sufficient resolution, such particles should appear as regular polyhedra rather than spheres, and have a mulberry-like surface (figure 14).

Results found to date bear out these expectations. For instance, one small spherical plant virus with a total molecular weight of 9 millions seems to have a protein shell containing 2×60 identical protein sub-units of molecular weight 57 000 arranged on the faces of a regular polyhedron. The RNA in the core is folded in a manner still unknown [16]. A larger insect virus (which contains DNA) can be clearly recognized as an icosahedron under the electron microscope [17].

Present observations thus lead one to conclude that small viruses consist of a core of nucleic acid which carries the genetic information, protected by a shell which is made up of many symmetrically arranged protein molecules of comparatively small size. The nucleic acid core carries the code for its own replication and for the manufacture of its protective protein, as well as for any enzymes required in one or other of these processes and not supplied by the host.

The microsomal particles associated with the synthesis of protein in normal cells appear to resemble the spherical viruses in shape and composition. This suggests that a virus infection may be equivalent to the injection of an apparatus for the manufacture of the wrong protein.

CONCLUSION

During the past six years molecular biology has changed from a subject of speculation and uncertainty to an exact science. Powerful methods of X-ray analysis have led to the elucidation of the basic molecular patterns of the most important types of protein fibres and of deoxyribonucleic acid; they are now beginning to reveal the structure of globular proteins and small viruses.

There is hope that genetic events in viruses and micro-organisms may soon be understood in molecular terms. A start has also been made in elucidating the genetic control and molecular mechanism of protein synthesis. Muscular contraction is another phenomenon which may soon be understood in molecular detail.

In many fields, on the other hand, knowledge of structure is still rudimentary and shows no correlation with our knowledge of normal and pathological function. Cell permeability and the whole problem of active transport through membranes is an important example. If the rapid development of molecular biology continues, these gaps may gradually be filled, and more and more of the fundamental workings of living systems may become understood in terms of the interaction between molecules of known structure, to the great benefit of biology and medicine.

REFERENCES

[1] WATSON, J. D. and CRICK, F. H. C. *Nature, Lond.*, **171**, 737, 964, 1953.

[2] FRANKLIN, R. E. and GOSLING, R. G. *Nature, Lond.*, **171**, 740, 1953.
WILKINS, M. H. F., SEEDS, W. E., and WILSON, H. R. *Ibid.*, **171**, 738, 1953.

[3] BENZER, S. in 'The Chemical Basis of Heredity'. W. D. McElroy and B. Glass (Editors). The Johns Hopkins Press, Baltimore. 1957.

[4] FELSENFELD, G. and RICH, A. *Biochim. Biophys. Acta*, **26**, 457, 1957.

[5] PALADE, G. E. *J. Biophys. Biochem. Cytol.*, **1**, 59, 1955.

[6] HOAGLAND, M. B., KELLAR, E. B., and ZAMECNIK, P. C. *J. biol. Chem.*, **218**, 345, 1956.

[7] RYLE, A. P., SANGER, F., SMITH, L. F., and KITAI, R. *Biochem. J.*, **60**, 541, 1955.

[8] CRICK, F. H. C. and KENDREW, J. C. *Adv. Protein Chem.*, **12**, 133, 1958.

[9] GREEN, D. W., INGRAM, V. M., and PERUTZ, M. F. *Proc. roy. Soc., A*, **225**, 287, 1954.

[10] KENDREW, J. C., BODO, G., DINTZIS, H. M., PARRISH, R. G., and WYCKOFF, H. *Nature, Lond.*, **181**, 662, 1958.

[11] CULLIS, A. F., DINTZIS, H. M., and PERUTZ, M. F. *Conference on Haemoglobin, Washington, Nat. Acad. Sci. and Nat. Res. Counc. (NAS–NRC publ.* 557), 1957.

[12] BODO, G. *Nature, Lond.*, **176**, 829, 1955; *Biochim. Biophys. Acta*, **25**, 428, 1957.

[13] HUXLEY, H. E. *Endeavour*, **15**, 177, 1956. See also *J. Biophys. Biochem. Cytol.*, **3**, 631, 1957.

[14] INGRAM, V. M. *Nature, Lond.*, **180**, 326, 1957; HUNT, J. A. and INGRAM, V. M. *Nature, Lond.*, **181**, 1062, 1958. See also INGRAM, V. M. *Sci. Amer.*, **198**, 68, 1958.

[15] BROWN, H., SANGER, F., and KITAI, R. *Biochem. J.*, **60**, 556, 1955.

[16] CRICK, F. H. C. and WATSON, J. D.; CASPAR, D.; FRANKLIN, R. E., KLUG, A., and HOLMES, K. C. in 'The Nature of Viruses'. G. E. W. Wolstenholme and E. C. P. Miller (Editors). J. and A. Churchill Ltd, London. 1957.

[17] WILLIAMS, R. C. and SMITH, K. M. *Biochim. Biophys. Acta*, **28**, 464, 1958.

Chemistry and alchemy in sixteenth-century Cracow

WŁODZIMIERZ HUBICKI

The history of early chemistry in Poland is very little known, but there was a period, the sixteenth century, when Cracow was one of the centres of alchemy and chemistry. This article surveys the state of these subjects at this time. It includes a description of an early instance of a claim to have produced gold by transmutation being put to the test of quantitative analysis.

Cracow, the capital of Poland in the middle ages, has one of the oldest of the Central European universities; it was founded in 1364. During the sixteenth century there probably were schools of the various branches of magic—Faust started his researches there [1]. These studies were, even if unsuccessfully, forbidden by the University, which was, however, a renowned centre for its officially recognized work in astrology and alchemy. The Cracovian astrological calendars had a European reputation until the seventeenth century, and the alchemical schools were of comparable repute.

It is easy to see why 'practical alchemy,' the precursor of chemistry as opposed to the alchemy of the philosopher's stone and the elixir, should have such importance in sixteenth-century Poland. The time was one of vigorous mining activity, of the establishment of the silver mines of the Tatra Mountains, new lead mines near Olkusz, and copper, brass, and lead foundries [2]. Cracow was the centre of this mining and metallurgy.

One of the most important foundries—a contemporary tells us it 'gave off smoke like Ætna'—was at Mogila, just outside Cracow. It was established by Jan Thurzo, and produced copper that was exported to Flanders, France, and Britain. The Royal Mint at Cracow used silver obtained from this copper ore for its coins, and in 1516 a royal decree established a laboratory.

This 'Camera Separatoria' was to study the separation of the precious metals and the manufacture of the fluxes and acids needed. It was directed by Kasper Ber, a Cracovian, as was Thurzo. Ber's reputation as a metallurgist was already sufficiently high for him to have students from Hungary, Germany and Bohemia.

Agricola [3] describes the Polish cupellation method, possibly devised by Ber, and also describes the Polish method for the extraction of lead [4].

That Agricola should describe the Polish techniques of extraction shows that they were fairly elaborate. The Poles were also surprisingly far advanced in assaying methods. A royal decree of 1555 laid down that pure tin, imported from Saxony or England, was to be marked with the king's initials and a crown. The purity, for these purposes, was measured by comparing the specific gravity of a sample with that of pure tin.

This method hardly suggests an exact science, but, in general, assaying methods were highly accurate. The balance was of striking importance even at this time, and many sixteenth-century assaying textbooks describe its construction. A typical book is that of C. Schreittmann [5]. He not only describes the balance, but also goes into detail about the weights, stating that they should be made of silver, kept in special boxes, and touched only with tweezers. It is a highly practical book, despite his referring to his smallest weights as atoms, as light as 'dust seen in the sunshine'.

Agricola, again, describes the care to be used in weighing [6]. 'It is necessary that the assayer who is testing ore or metals should be prepared and instructed in all things necessary in assaying, and that he should close the doors of the room in which the assay furnace stands, lest anyone coming at an inopportune moment might disturb his thoughts when they are intent on the work. It is also necessary for him to place his balances in a case, so that when he weighs the little buttons of metal the scales may not be agitated by a draught of air, for that is a hindrance to his work.'

His description [7] of the method of gold assay is interesting. 'One drachma [about 3·6 g] of examined sample was smelted together with 1 ounce [about 30 g] of lead with the addition of flux that is so-called artificial salt. The melted-out grain of gold was weighed. The next step was the determination of the quantity of silver in gold, which was done by means of touchstone and

FIGURE 1 – *The Polish hearth for lead smelting* [4]. *V, Polish hearth; P, Westphalian method of melting; Q, heaps of charcoal; R, straw; T, crucibles.*

assaying needles, or by etching it with nitric acid. The silver ore was determined by means of cupellation with lead.' The accuracy of these techniques is very striking.

Some sample alloys are preserved, together with the analyses by one of Kasper Ber's students. I have shown that, in fact, these results differ by less than one per cent from results obtained nowadays. This kind of accuracy needed extremely pure reagents. Nitric acid containing chlorides, for example, would lead to the dissolution of the gold as well as hindering that of the silver. The acid was purified by distillation over silver filings.

FIGURE 2 – *The Polish cupellation furnace in the sixteenth century* [3]. *A, furnace similar to an oven; B, passage; C, iron bars; D, hole through which the litharge is drawn out; E, crucible with dome removed; F, thick sticks; G, bellows.*

The representative, not to say originator, of another approach to chemistry arrived in Poland during this period. Paracelsus came to Poland about 1520, and had a medical practice in Cracow—he is recorded as curing the son of a rich Cracovian, Francis Boner. The prescription was *oleum philosophorum*, produced by distilling vegetable oil with powdered brick.

Little is known about Paracelsus's actual students. We know, however, that two of them, David Meyer and the court physician Albert Baza, were Poles. We have not much information about their activity; the Paracelsan group of the 1560s has left more traces.

Cracow was then one of the great centres of the movement—Paracelsus lived at Wroclaw [Breslau], immediately before his death, but there were lively commercial and intellectual contacts between the two cities.

The group at Cracow talked of alchemy, but not in the sense of transmutation. Thus Adam Schröter, from Nissa, writes: 'Only idiots think that alchemy is the knowledge of obtaining gold. The aim of alchemy is to look for new medicines.' It is Schröter, too, who gives a fascinating description of the famous Wieliczka salt mines in Paracelsan terms [8], where he states that the salt comes from the three '*principia*', salt, sulphur, and mercury. Salt, he says, has many uses, such as melting ores and gold, or preparing '*aurum potabile*', the elixir, adding that having mentioned this 'he must finish the wise words, for not everybody may know the sacred mysteries of salt.' He was less mysterious about the oil found in these mines. 'Petroleum, believe me, is very important, especially when it combines with salt. The good God gave our country petroleum. Poland, country of riches, you arouse admiration everywhere.'

It was also Schröter, backed financially by Albert Łaski, a rich Polish palatine, who enormously helped the spreading of the Paracelsan theories by translating his *Archidoxae* and *De praeparationibus* from the comparatively little known German into Latin.

Another distinguished Paracelsan, a pupil and follower of Copernicus living for some time at Cracow, was Joachim Rheticus. He wrote, in 1567, to Joachim Camerarius, a professor in Leipzig, 'I have lately had news of a new German medical school, followers of Theophrastus. I met and spoke with Theophrastus himself in 1532. He certainly was a great man and published splendid work. . . . I am interested in chemistry and

astronomy, but it is by medicine that I live.' His interest in chemistry is shown by another letter to the French philosopher Peter Ramus, where he said: 'As I am especially interested in chemistry, I have investigated its foundations and written seven books on it' [9].

There were other followers of Paracelsus in Cracow. Mardocheus Nelle, a Jewish physician, wrote a treatise on 'cements' (fluxes is the modern term), which was a commentary on *De transmutationibus metallorum* of Paracelsus; others were Jan Miączynski, a professor of medicine in the University of Cracow, who wrote a paper on the production of sulphuric acid from vitriol, and another professor, Kasper Skarbimirski, who edited a treatise *Epistolae alchemicae*.

Oddly enough, the greatest of the Paracelsans of that time is now almost completely unknown. This was Alexander Suchten [10]. He was the son of a rich and influential citizen of the port of Gdansk [Danzig]. Suchten himself is mentioned in the *Album diligentarium* of the University of Cracow as 'Alexius Zuchta de Gedano alias etiam Suchten dictus Kaszuba Polonus' who lectured 1521–22. In 1539 he was a canon at Frombork [Frauenburg], at the same time as Copernicus. He then studied in Louvain and in Italy and by 1549 he was librarian to Otto Heinrich, one of the electors of the Palatinate. Here he collected alchemical books, probably became acquainted with the works of Paracelsus, and gained a large following of students. In 1554 he returned to Cracow, eventually to become physician to King Sigismund Augustus; he left Poland in 1563, and went to the court of Prince Albert of Prussia, at Königsberg, and in about 1570 he went to Strassburg, where he printed his first works on antimony.

Suchten was a prolific writer of poems, theological dissertations, and treatises on chemistry and medicine. Among his most important works are *Liber unus de secretis antimonii* and *De antimonio vulgari*. These, and other works, have been translated into English by Cable in 1670 and A. Waite in 1893. He styled himself 'Chymicus' and referred to those attempting transmutation as alchemists, though he was expert in many of the alchemical techniques of distillation and purification and in several of his experiments clearly hopes to be able to show transmutation. He gives [11] accounts of the testing of some 'alchemical silver' which turned out to be an alloy of antimony, and of some alchemical gold that had been considered genuine by a goldsmith, a view which Suchten himself thought, at one stage, he had confirmed.

This experiment is extremely interesting, because it is the first published account of an experimentally proved refutation of transmutation by use of a balance. He says [the quotation is from Cable's translation]: 'Now come I to ☉,[1] and to tell you what happened to me is a wonder; when I had shewed to my good Companion, who thought nothing else but that he had got a great prize, he would not believe it, but took it into his own hands and at length found the truth, and began to question his ☉, and he spake, although I have often times tried it yet will not I trust myself, but take this half ounce of Gold and try it as you please. Mr *Hans* the Goldsmith saith it is true Gold. So took I the ☉ and brought it to the Goldsmith, and asked him if it were Gold, he said it was, and he could work it for ☉; for to the Sight, Touchston and Hammer it was very good ☉. Nevertheless I took the ☉ and did put to it 2ʒ of ☾ to granulate and divid it in *aq. fort.* the ☾ dissolved it self, the ☉ fell to the bottom; this proof was true; this *sol* powder I mixed with ♁ crude and cast it through *Regulus*; let it flow in a Crucible and cast *Nitre* upon it, and drew the ♁ from the sol, and drew it off with ♄, this trial I found it also true. This *Sol* driven off did I cast again through, with ♁ and ♳; then took I the *Regulus* and let them go away before the Goldsmiths Bellows, for I had none; this trial the *Sol* stood also, on which every Chymist may justly rejoice.

'Nevertheless seeing the *Luna* had deceived me, therefore could I not trust the *Sol*, and caused it to be beaten thin, and amalgamated it with my ☿ of ♁, did set it four weeks in a gentle warmth, and took notice that the Amalgam was not hard, but soft, which was grievous to me; nevertheless I let it stand four weeks, and found my Amalgam much moister than when I put it in; then did I put it into a Crucible over a small fire, that the Crucible did not fully glow, and my ☿ flew away incredible swiftly from the ☉ that I did not mark it, but thought that my ☿ was coagulated into ☉, but when I weighed my ☉, I found no more than half an Ounce and 2 Quintileins [2 drams], and thought certainly that the two Quintileins were pure Gold.

'These two Quintileins I proved farther with ☿ of ♁ in the same manner as at the first time; then after that I evaporated the *Mercury* from it, and

[1] At this time the names of the substances, their astronomical names, and the astrological symbols were used indifferently. In this extract the symbols are to be interpreted as follows: ☉, *Sol*, Sun, gold; ☾, *Luna*, Moon, silver; ♁, antimony; ♄, Saturn, lead; ♳, sulphur; ☿, mercury.

found my two Quintileins again; then was I merry, and hoped that my Companion would communicate his Preparation to me and I had Golden Mountains in my head, and I brought a good Message to my Companion, but he himself was not merry, but spake evil of it. *Well*, said he, *I have had great labour and pains with this* ☉, *and more than I do say. . . . The Gold which remaineth over and above to thee is not come from the Regulus, but is a composition of the Natural* ☉; *for I could not coagulate the Regulus into* ☉ *if there be not good Gold with it; thus Sol hath remained in the Test, but the other not, I know not how to bring it farther; and now understand the cause well, that that cannot be that I hoped.*'

His perseverance in the testing is impressive; his discovery that the substance was an alloy of gold was the result. He himself explains how there came to be any gold in the alloy—it had been added, a common technique of the alchemists, who assumed that the gold would grow, or multiply.

There was an anti-Paracelsan school. In Germany it was under the leadership of Thomas Erastus, in Cracow under Andrzej Grutyński, a professor at the University. Grutyński wrote two treatises, *Medicus dogmaticus* and *Solus philosophicus*, against Paracelsus, and these and similar books, and the books of Paracelsus and his followers, and the earlier works of Arnold de Villanova and Ramon Lull, were all to be found in two bookshops in Cracow that specialized in chemistry and alchemy, namely those of Zacheus Kessner and Johannes Thenaud.

Poland's importance in sixteenth-century political manœuvring caused a lively movement of people between Cracow and the main European towns. Thus Albert Łaski came to England in 1583 as a personal guest of Queen Elizabeth, and took part in a disputation at Oxford, in which Giordano Bruno defended his own and Copernicus's theories. He went to Kenilworth and worked with the alchemists John Dee and Edward Kelley, until his money ran out and he left, to avoid imprisonment for debt.

Łaski left in England his debts; he took with him John Dee and Edward Kelley, and their families. John Dee has left a description, in his memoirs, of a séance at the palace of the king, Stefan Batory, at Niepolomice, near Cracow. He made many other acquaintances in Cracow, among them Hannibal Roselli, the king's confessor and a publisher of hermetic books, and the professors of Cracow.

There was thus an enormous interest in alchemy in Cracow, by kings (such as Sigismund Augustus, Stefan Batory, and Sigismund III) as well as bishops (e.g. Krasński and Padniewski), noblemen, and the rest of the citizens. There were charlatans and their dupes, but, steadily, there was the voice of reason. There were sermons against the swindlers; Grutyński [12] wrote: 'A chemist looks for the right heat to make gold but, from the nature of metals, we know he cannot make gold but only a substance looking like gold. There is an eternal difference between natural gold and these mixtures. It is stupid and silly to sweat in smoke, to waste time and money in this way.'

Suchten, too, attacks Lull, supposed to have made the gold from which Edward III made rose nobles. This legend bristles with anachronisms, but Suchten attacks the practicability of the preparation in his *Elegia de Nobel Raymundi moneta Anglicana* [13]:

'. . . Ex aliis aurum nunquam fecisse metallis
Creditur, aut pueros hoc docuisse suos.
. . . Lulle valete,
Nobile Raymundi vana moneta tua est.'

REFERENCES

[1] WIER, J. 'De praestigiis daemonum et incantationibus . . .'. Basle. 1564.

[2] HUBICKI, W. *Ann. Univ. M. Curie-Skłodowska, Sec. AA*, 10, 7, 1955.

[3] AGRICOLA, G. 'De Re Metallica', translated from the first Latin edition of 1556 by H. C. Hoover, p. 483. London. 1912.

[4] *Idem. Ibid.*, p. 392.

[5] SCHREITTMANN, C. 'Probierbüchlein . . .', p. 18. Frankfurt am Main. 1580.

[6] AGRICOLA, G. 'De Re Metallica', p. 223. London. 1912.

[7] HUBICKI, W. 'Georgius Agricola' (in Polish). Pp. 104–30. Polish Academy of Science. Wrocław (Breslau). 1957.

[8] SCHRÖTER, A. 'Regni Poloniae Salinarum Vieliciensium Descriptio'. Cracow. 1554.

[9] RHETICUS, J. Library of the University of Erlangen, Cod. Ms. Trew's Collection. 1821.

[10] HUBICKI, W. 'Dr Al. Suchten the Forgotten Chemist' (in Polish). Studia i Materiały z dziejów nauki polskiej. Pp. 102–120. Polish Academy of Science. Warsaw. 1953.

[11] SUCHTEN, A. 'Chymische Schrifften alle . . .', p. 295. Frankfurt am Main. 1680. [The quotation is actually from the English translation by Cable 'Alex von Suchten of the secrets of antimony in two treatises'. London. 1670.]

[12] GRUTYŃSKI, A. 'Medicus Dogmaticus'. Cracow. 1598.

[13] SUCHTEN, A. 'Chymische Schrifften alle . . .', p. 489. Frankfurt am Main. 1680.

Trapped radicals

H. P. BROIDA

The theory of chemical reactions was vigorously stimulated by the realization that the products are the result of complex intermediate reactions, often involving free radicals. The study of these is handicapped by their reactivity and the small concentrations in which they occur, and it was not until recently that low-temperature physics and techniques of structural investigation were combined to study free radicals fixed in inert solids. The techniques that are used and the results of the study of these trapped radicals are discussed here.

One of the great contributions to scientific thought in the last half-century has been the realization that chemical reactions occur in a series of very definite steps. Although Arrhenius had indicated the importance of sufficient energy being available for reactions to take place, it was not until the 1920s that the detailed manner in which chemical reactions occur began to be widely interpreted in terms of molecular structure. Developments in the kinetic method, coming simultaneously with advances in theoretical chemistry and physics, revealed the importance of the fine details of reactions. It was realized that even relatively simple reactions such as the formation of water from hydrogen and oxygen actually were achieved by a complex series of intermediate steps. The overall reaction is made up of a large number of elementary reactions quite often involving highly reactive intermediates which normally have very short lifetimes. Free radicals are one important class of these intermediates.

A free radical is a chemical fragment—either atomic or molecular—which has an unpaired electron spin. The reactivity of the radical is due to the unpaired electron and, except in very unusual cases, such as large aromatic radicals which are stabilized by resonance, the lifetime of these species is considerably less than one second. Because of their high reactivity the concentrations of free radicals are generally very small, except at very high temperatures.

The problem of studying the structure and the properties of free radicals and their reactions is made very difficult by this high reactivity, the short lifetime, and the small concentrations which can be obtained. Nevertheless considerable information has been acquired by a variety of methods [1]. Deductions made from kinetic observations of reactions undergone by radicals have been particularly fruitful. Light emitted and absorbed by radicals, particularly in flames and hot gases, also has given considerable information [2]. Under some conditions it has been found possible to withdraw radicals from a chemical reaction into a mass spectrometer [3].

In recent years a number of workers more or less simultaneously decided to investigate the possibility, envisaged by G. N. Lewis [4] in 1941, of preserving radicals of low molecular weight by surrounding them with a rigid environment of molecules or atoms with which reactions could not occur. The results of these studies have demonstrated that highly reactive radicals can be trapped in solids at low temperatures [5] in concentrations near 1 per cent.

HISTORICAL ASPECTS

Radicals were first trapped inadvertently by many investigators who were interested in other problems. Three rough subdivisions of the historical background can be made: the first, going back to before the turn of the century, saw the development of very low temperature techniques and their application to observations on solidified gases; the second period started in the 1920s with the studies of reactions of radicals on cold surfaces; and the third phase began early in the 1950s with the application of a number of techniques of modern technology.

The first observations involving trapped radicals were probably made by J. Dewar in London, who reported various bright flashes and beautiful colours in products formed by the ultra-violet irradiation of a number of solids at liquid air temperatures [6]. R. J. Strutt [7] in 1911 unsuccessfully tried to trap at the temperature of liquid air the active species in the afterglow of a discharge through nitrogen. Between 1924 and 1935 L. Vegard, working at Leiden and at Oslo, made extensive investigations of the spectra emitted by condensed gases at temperatures down to 4·2° K when bombarded by electrons and ions [8]. His interest centred mainly on postulated explanations,

including free radical reactions, of astronomical phenomena such as the aurora borealis. Similar studies were independently done by J. C. McLennan in Toronto [9].

The second stage is concerned with the development of chain mechanisms involving free radicals and with the effects of cold surfaces on these mechanisms. M. Bodenstein and F. Haber were active in this field. Later they were joined by Geib and Harteck, who became interested in the formation of hydrogen peroxide at low temperature. This work, involving the condensation of products of electrical discharges through water vapour, hydrogen peroxide vapour, hydrogen mixed with oxygen, and ammonia occupied the attention of others, including O. Oldenberg, W. H. Rodebush, Poljakow, G. I. Lavin, and J. R. Bates. In more recent years this phase has merged with the investigations of P. A. Giguère and of C. A. Winkler [10], who used discharge products, and of Everett and G. J. Minkoff, who have rapidly chilled explosion products.

The third and current phase was initiated by the work of F. O. Rice, who was probably the first to start with the aim of retaining highly reactive free radicals in solids and to show definite evidence of unstable chemical species being trapped on cold surfaces as a result of rapid cooling and condensation of decomposed parent compounds [11]. The development of physical methods of detection of free radicals—such as electron spin resonance, magnetic susceptibility, optical spectroscopy, and mass spectroscopy—has greatly accelerated the interest in studying solids in which radicals are trapped.

EXPERIMENTAL TECHNIQUE

It will be convenient to illustrate the types of phenomena which have attracted so much attention by using as examples some of the more vivid experiments. Discharge products of nitrogen when condensed at very low temperatures (below 25° K) give rise to some spectacular features. Moreover, these experiments, while simple enough to be easily reproduced, are indicative of the techniques and problems encountered in the studies of trapped radicals. For these reasons the method will be described in some detail.

Nitrogen gas at a pressure near 1 mm Hg passes through an electrodeless discharge (125 watt, 2450 Mc/s). The discharge products, mainly nitrogen atoms and molecules, are pumped in less than 0·1 sec to a Pyrex surface kept near 4·2° K by liquid helium (figure 6).

Discharge products of nitrogen have been studied for many years [12] and are known as 'active' nitrogen. In a darkened room this 'active' gas can be seen as a yellow glow filling the tube downstream from the discharge (figure 5). When the 'active' nitrogen impinges on the cold surface a bright, warm green glow immediately appears (figure 7). When the 'active' nitrogen stream is removed, a green glow (afterglow) persists on the cold solid for several minutes (figure 8). Either during deposition or after this glow has disappeared, a white solid (figure 9) can be seen with reflected light. If the solid is warmed to about 10° K the solid again begins to glow (warm-up glow), emitting green light (figure 14). Further warming to about 30° K causes a blue glow (figure 17). If argon is present, the deposited solid often peels away from the Pyrex surface (figure 18) after the glow has stopped.

The addition of small amounts of oxygen before the discharge causes the green glow to become more yellow (figure 11). This effect is more pronounced at higher temperatures. If the concentration of oxygen is greater than a few per cent, the glow of the solid is extinguished. When an excess of argon is added to the nitrogen, the glow from the solid during deposition is blue (figure 12). At high gas-flow rates a weak glow is sometimes observed in the gas near the solid (figure 19).

While the deposition proceeds, vivid blue and yellow flashes also occur on the solid. Colour photographs taken at 16 frames per second indicate that the flashes develop locally. On some occasions small spots of intense reaction are observed to travel fairly rapidly through the solid (figure 20). These regions are fairly reproducible. The reproducibility probably is due in part to temperature gradients and in part to imperfections in the solid. At times the heat liberated is so great that all the reactive products are destroyed and the light given off is enough to over-expose completely a single frame of the film.

To consider the light emission in more detail, it is useful to see the spectra obtained under various conditions. Figures 2–4 present spectra obtained during deposition of discharged nitrogen. The brightest features are the α (green) and the β (yellow) systems, which are shown in more detail in figure 3. The strong α group, consisting of a close set of five sharp lines near 5230 Å, is almost certainly emitted by nitrogen atoms. This transition is from the ^2D electronic state to the ground ^4S state. The weaker α′ and very much weaker α″ groups (figure 4*a*) occur when the α

group is strong and may be associated with a loosely bonded complex of N and N_2. The β group, consisting of three diffuse lines near 5575 Å, probably is the ^1S–^1D transition of atomic oxygen. Between 3572 and 6390 Å the sharp-headed A bands are observed (figures 2*b*, 4*b*). The broad B bands (figures 2*c*, 4*c*) are of unknown origin, although it is possible that they are associated with NO_2. With excess argon present the blue emission (figure 1*a*) is caused by a series of sharp bands starting at 4450 Å and extending into the ultraviolet (figure 2*d*). These bands are known as the Vegard-Kaplan system and are the $A^3\Sigma$ to $X^1\Sigma$ transition of molecular nitrogen. These bands also are emitted during the blue warm-up (figure 1*c*) when excess argon is present. When there is less than 20 per cent nitrogen in the argon, an unidentified molecular band system appears relatively strongly (M bands in figures 2*d* and 4*d*). Argon also causes a shift in position of the β lines and a large change in the relative intensities of the α lines (figure 3).

When the nitrogen deposition ends and the solid begins to warm up there are large changes in the spectrum, as shown in figure 2*e*. The first few flames after termination of the discharge (afterglow, figure 1*d*) show the α lines of atomic nitrogen to be diminishing in intensity (flames 1–6, figure 2*e*). However, as the liquid helium disappears (flame 6), the intensity of the α group increases, together with the β lines of atomic oxygen, giving the green warm-up glow (figure 1*e*). At temperatures above 25° K the β bands begin to decay, causing the blue warm-up glow (figure 1*f*). Above 30° K the emission is greatly diminished (flame 18, figure 2*e*).

During the warm-up of the discharge nitrogen products condensed at 4·2° K considerable amounts of heat are evolved. If it is assumed that this heat release is caused by the recombination of nitrogen atoms, the number of nitrogen atoms trapped in the solid can be measured. Thus far, only unusual and low-yield calorimetric techniques have been employed because of the restrictions imposed by the procedure of trapping gas discharge products. Good thermal contact with the 4·2° K reservoir during deposition is essential to avoid losing the active species at higher temperatures. In addition, during warm-up of the solid deposit, the calorimeter needs to be thermally isolated. Moreover, a relatively large opening into the calorimeter is needed for bringing in the 'active' nitrogen without destroying the active species. These requirements are not easily met, and a compromise has to be made. One calorimeter rapidly warms the solid with electrical heating and compares the time for the solid discharged nitrogen to reach a fixed 'high' temperature with the time for the same mass of undischarged nitrogen. Typical curves for such times of warming are shown in figure 1. The discharged nitrogen warms up more rapidly and leads to an atom concentration of a few per cent [13].

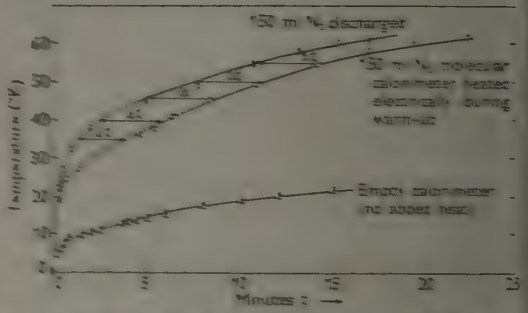


FIGURE 1 – *Warm-up curves for discharged and molecular nitrogen (heated electrically) and empty calorimeter.*

PRESENT KNOWLEDGE OF TRAPPED RADICALS

It is important to emphasize that the subject of trapped radicals is a new one and in a state of rapid development. Undoubtedly, therefore, in the next few years there will be considerable modification of the details of the brief review included here. However, the major conclusions should remain: (1) free radicals, made in a variety of ways, can be trapped in solids at low temperature; (2) these radicals can be preserved for indefinitely long times at low enough temperatures; and (3) heat, light, and chemical reactions can be obtained at low temperatures from these trapped radicals.

Good evidence has been reported for the trapping of three atomic free radicals: H, N and O. Electron spin resonance presents the most unequivocal evidence for the presence of unpaired electrons and thus proves that both H [12] and N [13] can be maintained in low-temperature solids. Nitrogen atoms, obtained from a discharge through nitrogen gas before deposition, have been observed with estimated concentrations near 0·1 per cent in solid N_2 at 4·2° K. Various solid acids at 77° K have been irradiated with γ-rays from cobalt 60 and show that H atoms are trapped, also the concentrations of atoms are unchanged after several months' storage at 77° K. Optical emission spectroscopy has indicated the presence of trapped N and O [26]. Chemical

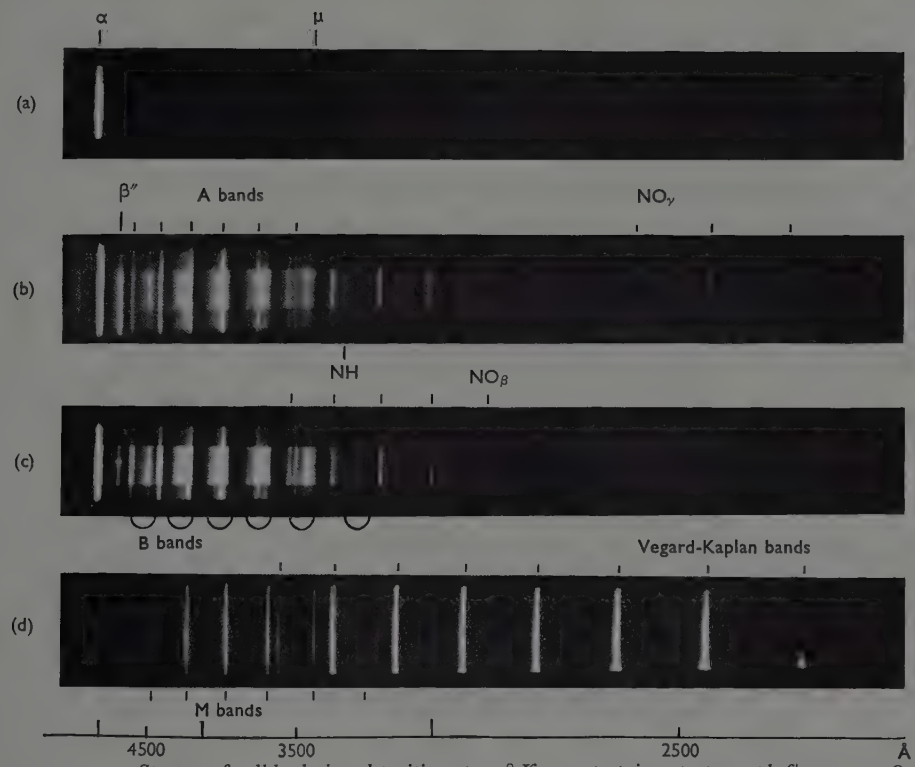


FIGURE 2 – *Spectra of solids during deposition at 4·2° K; quartz prism spectrograph f/4; 102 a-O plates.* (a) *Pure nitrogen; gas flow rate 1·5 cm³/sec; exposure times 1 min. and 3 min.* (b) *Commercial nitrogen; gas flow rate 1·5 cm³/sec; exposure times 1 min and 3 min.* (c) *Pure nitrogen with 0·1% oxygen added; gas flow rate 1·5 cm³/sec; exposure times 1 min. and 3 min.* (d) 5% *nitrogen–95% argon mixture; gas flow rate 2 cm³/sec; exposure time 3 min.*

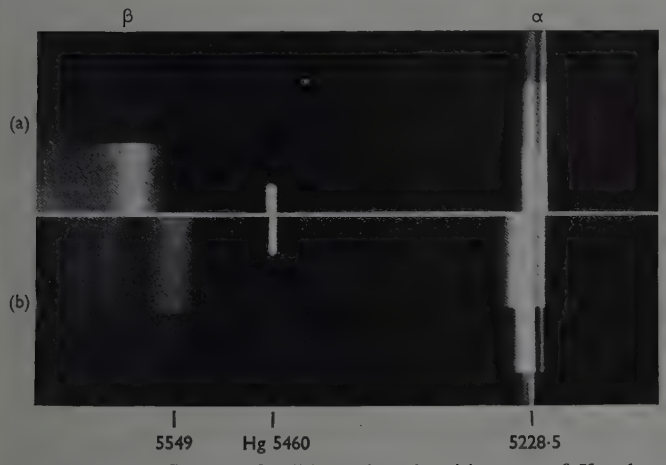


FIGURE 3 – *Spectra of solids during deposition at 4·2° K; glass prism spectrograph f/10; 103 a-F plate.* (a) 5% *nitrogen–95% argon mixture; gas flow rate 2 cm³/sec; exposure times 7, 14, 23 min.* (b) *Pure nitrogen with 0·1% oxygen added; gas flow rate 1·5 cm³/sec; exposure times 3, 9, 27 min.*

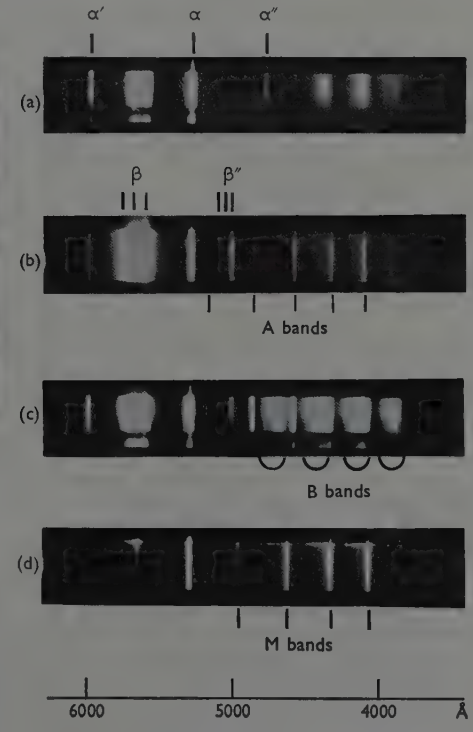


FIGURE 4 (*right*) – *Spectra of solids during deposition at 4·2° K; glass grating spectrograph f/0·625; 103 a-F film.* (a) *Pure nitrogen; gas flow rate 1·5 cm³/sec; exposure time 80 sec.* (b) *Commercial nitrogen; gas flow rate 1·8 cm³/sec; exposure time 5 sec.* (c) *Pure nitrogen with 0·1% oxygen added; gas flow rate 1·5 cm³/sec; exposure time 80 sec.* (d) 5% *nitrogen–95% argon mixture; gas flow rate 2 cm³/sec; exposure time 5 sec.*

FIGURE 5 – *Gas afterglow from discharge through nitrogen with a small impurity of oxygen.*

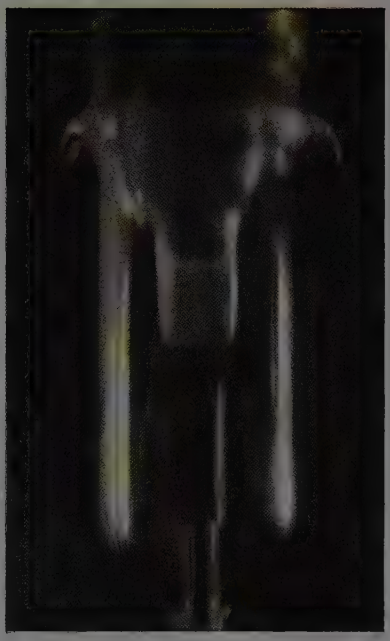


FIGURE 6 (*right*) – *Pyrex surface upon which discharge products are condensed. Liquid helium is beginning to fill the chamber.*

FIGURE 7 – *Nitrogen, discharge on.*

FIGURES 7–20 – *Colour photographs*[1] *of glows produced from solids condensed from discharges through nitrogen gas mixtures. Exposure times are usually of one second.*

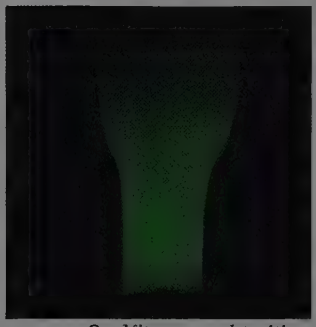


FIGURE 8 – *Nitrogen, no deposition, discharge off, afterglow.*

FIGURE 9 – *White solid as seen with reflected light.*

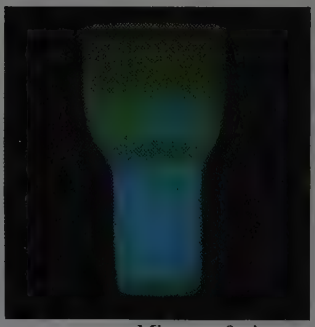
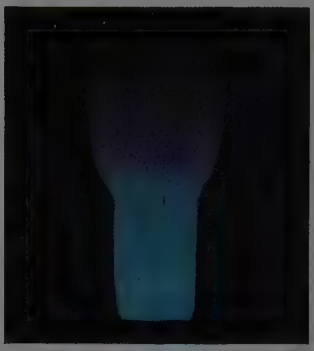


FIGURE 10 – *Mixture of nitrogen and argon, discharge on.*

FIGURE 11 (*left*) – *Nitrogen with small amount of oxygen, relatively high flow rate, discharge on.*

FIGURE 12 (*right*) – *Nitrogen with an excess of argon, discharge on.*



[1] *The colour photographs were made by Mr Warren P. Richardson, Photographic Services Section, National Bureau of Standards.*

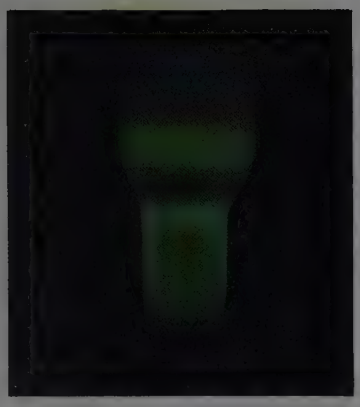


FIGURE 13

FIGURE 14

FIGURE 15

FIGURE 16

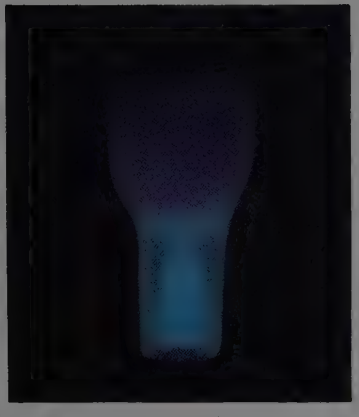


FIGURE 17

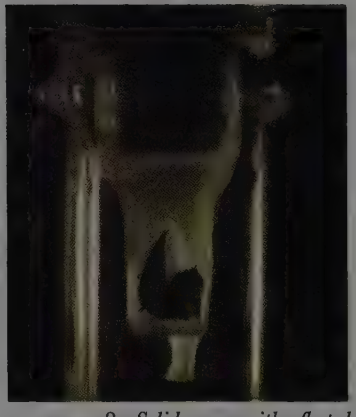


FIGURE 18 – *Solid as seen with reflected light shortly after figure* 17 *was obtained.*

FIGURES 13–18 – *Sequence of photographs taken immediately after figure* 10 *in approximately* 5*-second intervals during the warm-up of a mixture of nitrogen and argon. No gas flow.*

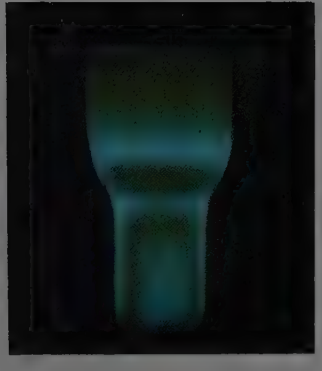
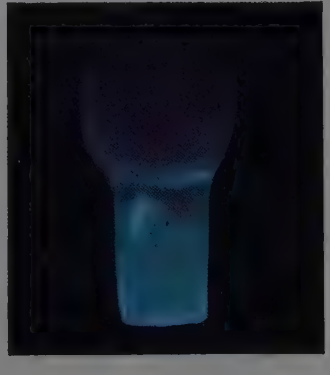


FIGURE 19 (*left*) – *Nitrogen and argon at high flow rate, discharge on.*

FIGURE 20 (*right*) – *Blue flash observed during deposition; exposure time of approximately* 1/25*th sec.*



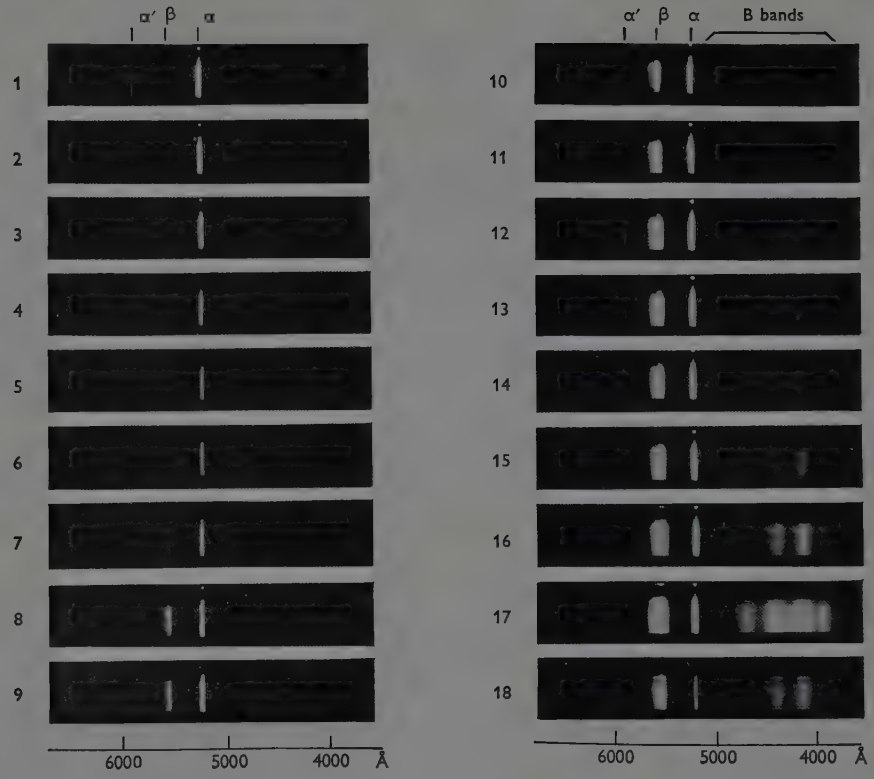


FIGURE 21 – *Spectra recorded during the afterglow and the warm-up of solid nitrogen containing* 40% *argon; glass grating spectrograph f*/0·625; 103 *a-F film; each frame is* 10 *sec exposure with* 5 *sec between consecutive frames. Frames* 1–6, *afterglow;* 7–16, *yellow-green warm-up period;* 17–18, *blue period.*

evidence [17], that is the interpretation of the products obtained on warming solids containing discharge products, supports the view that several per cent of these atomic radicals are trapped in solids below 20° K. Calorimetric experiments also indicate the presence of several per cent of both N and O [13].

The NH radical in solids has been the subject of many investigations. Rice and his co-workers [11] have studied extensively the products of hydrazoic acid decomposed by photolysis, pyrolysis, and electrical discharges. When such products are condensed on a surface cooled to 77° K a bright blue deposit is formed. This solid changes abruptly to white at 150° K, and sometimes the change in colour is accompanied by a violent explosion. Deductions from the compounds formed, supported by evidence from infra-red and ultra-violet absorption, indicate that NH radicals must have been present at some stage. The failure to find NH by mass spectrometry in the gas prior to deposition of the blue solid suggests that the concentration of NH in the solid is very small.

Many organic radicals have been trapped and detected both by optical spectroscopy and electron spin resonance. I. Norman and G. Porter [18] prepared a number of trapped radicals in 'glasses' of solid hydrocarbons at 77° K by photolysis with ultra-violet light and detected their presence by ultra-violet absorption spectroscopy. A large varity of organic radicals have been prepared by photolysis and detected by their free electron spins, using electron spin resonance. Usually the spectra are so complicated that specific identifications of the radical have not been possible. However, methyl, ethyl, and allyl radicals [19] have been positively identified as trapped in various solids.

PRESENT POSITION AND FUTURE PROSPECTS

During recent years the realization of the

interesting potentialities of trapped radicals has led many investigators into this new field, and detailed attacks on the subject are now in progress. The broad plan involves, first, studies of methods of producing trapped radicals. Investigations are under way of the uses of pyrolysis, electric discharges, and chemical reactions to produce free radicals in the gas, followed by rapid cooling and condensation. Another approach is to use photolysis, γ-irradiation, or high-energy particle bombardment to produce the radicals directly in a cold solid.

Secondly, there are the problems associated with the detection and the measurement of the concentration of the trapped radicals. Electron spin resonance, optical spectroscopy (from 1400 Å to 25 μ), and calorimetry have been the most productive methods and are the methods most extensively being applied. However, instruments for mass spectroscopy, magnetic susceptibility, X-ray diffraction, electron diffraction, and dielectric measurements are being constructed and will soon be applied to this problem.

The third broad aspect of the field involves the problems of what takes place as the solid containing trapped radicals is brought to higher temperatures. Chemical methods are being developed for analysing the products, and the usual methods of chemical kinetics are being extended to lower temperatures to determine intermediate reactions. Information obtained by studying the relationships between the heat released and the temperature changes during warm-up is being analysed to determine the diffusion rates and the types of species originally present in the solid. Radiation found during the warm-up helps in the understanding of the mechanisms of the reactions.

Finally, we may consider developments associated with the trapping of the radicals. Some ideas are beginning to evolve concerning the chemical, statistical, and solid-state factors which control the various phenomena. It appears that the use of free radicals as tracers will increase our knowledge of the solid state, since a definite perturbation, the free radical, can be introduced into normal, molecular, solids. In addition, a new field of low-temperature chemistry may evolve from the study of the reactions of trapped radicals. This may lead to the formation of new chemical compounds or known compounds by new methods. Another interest centres around the possible use as a propellent of energy stored in the form of trapped radicals, because of the definitely higher specific thrust available from mixtures containing large concentrations of free radicals of low molecular weight.

Many problems must be solved before the various phenomena associated with the trapping of free radicals can be controlled. However, it is just this lack of understanding which brings interest and excitement to the field. At this time work in this field shows great promise.

REFERENCES

[1] Steacie, E. W. R. 'Atomic and Free Radical Reactions'. Reinhold Publishing Corporation, New York. 1954.

[2] Gaydon, A. G. 'The Spectroscopy of Flames'. Chapman and Hall Ltd., London. 1957.
Porter, G. *Endeavour*, **16**, 224, 1957.

[3] Lossing, F. P. *Ann. N.Y. Acad. Sci.*, **67**, (9), 499, 1957.

[4] Lewis, G. N., Lipkin, D., and Magel, T. *J. Amer. chem. Soc.*, **63**, 3005, 1941.

[5] Broida, H. P. *Ann. N.Y. Acad. Sci.*, **67**, (9), 530, 1957.

[6] Dewar, J. *Proc. roy. Soc.*, **68**, 360, 1901.

[7] Strutt, R. J. *Ibid.*, **86**, 56, 1911–12.

[8] Vegard, L. *Ann. Phys.*, **6**, 487, 1930.
Vegard, L. and Stensholt, S. *Skr. norske Videnskap-Akad.*, **1**, (9), 1935.

[9] McLennan, J. C., Samson, E. W., and Ireton, H. J. C. *Trans. roy. Soc. Can.*, **23**, 25, 1929.

[10] Jones, R. A. and Winkler, C. A. *Can. J. Chem.*, **29**, 1010, 1951.

[11] Rice, F. O. and Freamo, M. *J. Amer. chem. Soc.*, **73**, 5529, 1951; **75**, 548, 1953.

[12] Mitra, S. K. 'Active Nitrogen—A New Theory'. Indian Association for the Cultivation of Science, Calcutta. 1945.
Berkowitz, J., Chupka, W. A., and Kistiakowsky, G. B. *J. chem. Phys.*, **25**, 457, 1956.

[13] Minkoff, G. J., Scherber, F. I., and Gallagher, J. S. (To be published.)

[14] Livingston, R., Zeldes, H., and Taylor, E. H. *Disc. Faraday Soc.*, No. 19, 166, 1955.
Jen, C. K., Foner, S. N., Cochran, E. C., and Bowers, N. A. *Phys. Rev.*, **104**, 846, 1956.

[15] Cole, T., Harding, J. T., Pellam, J. R., and Yost, D. M. *J. chem. Phys.*, **27**, 593, 1957.

[16] Herzfeld, C. M. and Broida, H. P. *Phys. Rev.*, **101**, 606, 1956.
Broida, H. P. and Peyron, M. *J. Phys. Rad.*, **18**, 593, 1957; **19**, 1958.

[17] Ruehrwein, R., Edwards, J. W., and Hashman, J. (To be published.)

[18] Norman, I. and Porter, G. *Proc. roy. Soc., A*, **230**, 399, 1955.

[19] Smaller, B. and Matheson, M. S. *J. chem. Phys.*, **28**, 1169, 1958.

Satellite tracking: its methods and purpose

E. G. C. BURT

The Earth satellites contain instruments for transmitting information about the conditions of outer space. Such information is more useful if the satellites can be precisely located during their circuits, and, in addition, this plotting of the paths provides valuable data about the Earth. The methods used and the results obtained are discussed in this article.

The advent of the Earth satellite as a space laboratory has revealed new possibilities for many branches of research: investigators of solar radiations, geophysical phenomena, and cosmic rays, to mention but a few, are all contestants for the limited space available in the satellite laboratory, and all rely on the efficient working of the instruments contained within it. There is, however, much to be gained from a knowledge of the satellite's course through space, which can be derived from ground observations independently of the orbiting instruments. Apart from its intrinsic worth, information about the orbit assists the interpretation of other data: measurements of temperature and of cosmic ray intensity, for example, are much more valuable if they can be related to a particular time and place.

RADIO METHODS

Many satellite tracking systems exist, all of which are useful in certain circumstances. If the satellite carries a transmitter, various radio methods are available for establishing its whereabouts. These techniques are particularly useful during the early life of the space vehicle, when little is known about its path; the transmitter advertises its position over a wide area, so that it can be located without previous knowledge of the approximate orbit.

Probably the simplest arrangement is that which employs the Doppler effect. If the satellite transmitter sends out a continuous, unmodulated wave at a fixed frequency, the signal received on the ground exhibits a change in frequency, due to the relative velocity of satellite and observing station. The received and transmitted frequencies f and f_0 are related by

$$f=f_0(1+\dot{s}/c)$$

where c is the velocity of light and s the distance between satellite and observer. If then the frequency is recorded as the satellite approaches and recedes, the radial velocity $\dot{s}$ can be calculated from

$$\dot{s}=c(f-f_0)/f_0$$

At the instant of closest approach the radial velocity will be zero, for then the relative velocity V_R is normal to the sight-line (figure 1); t seconds later the satellite will have moved a distance $V_R t$, so that

$$s^2=s_0^2+V_R^2t^2$$

where s_0 is the minimum distance. Differentiating this equation with respect to time gives

$$\frac{t^2}{\dot{s}^2}=\frac{s_0^2}{V_R^4}+\frac{t^2}{V_R^2}$$

and a graph of $t^2/\dot{s}^2$ against t^2 should therefore yield a straight line, from which V_R and s_0 can be derived. A typical result, obtained early in the life of Sputnik 1 (15th October 1957), is shown in figure 2. The Doppler measurements were made by the Post Office Radio Station at Banbury.

The orbital period can be found by observing successive transits at the same station. However, the period is not simply the difference between the times of closest approach: a correction must be applied to allow for the fact that, in the intervening period, the rotation of the Earth has altered the observer's position relative to the satellite's orbit.

The accuracy with which the orbit can be determined from Doppler data alone depends, among other things, on the separation between the satellite and the observing stations, and between the stations themselves. For favourable triangulation these distances should be of the same order, but this cannot be achieved without the active cooperation of the satellite unless a large number of stations is in operation. Over the distances involved (normally a few hundred kilometres) the curvatures of the orbit and of the Earth are too large to be ignored—a fact which greatly complicates the analysis.

Refraction of the radio waves in the ionosphere can lead to considerable errors, particularly at the lower frequencies [1]. The 20 Mc/s and 40 Mc/s transmissions of the first two Sputniks, for example, frequently gave very different estimates of the

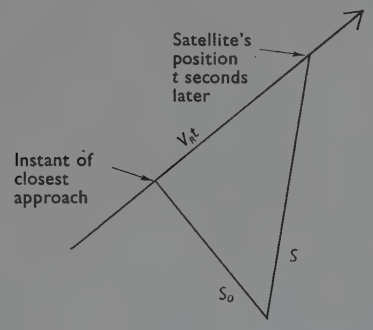


FIGURE 1 – *Relation between distance and relative velocity.*

satellite's position unless it happened to pass nearly overhead, in which case the electrical and optical paths are more nearly coincident. A much more satisfactory frequency—from the tracking standpoint—is the 108 Mc/s used in the American satellites; but of course the 20 Mc/s and 40 Mc/s transmissions of the Sputniks provide an excellent means of investigating ionospheric phenomena, particularly if the true path can be established independently.

A second tracking method which has been used successfully is the radio interferometer. Unlike the Doppler system, which measures radial velocity, the interferometer provides directional information, so that the two methods are complementary. As its name implies, the interferometer makes use of the interference pattern between the signals received at a pair of aerials, a pattern determined by the difference in the distance between the satellite and each of the receiving aerials. The separation between the aerials—say 50 to 100

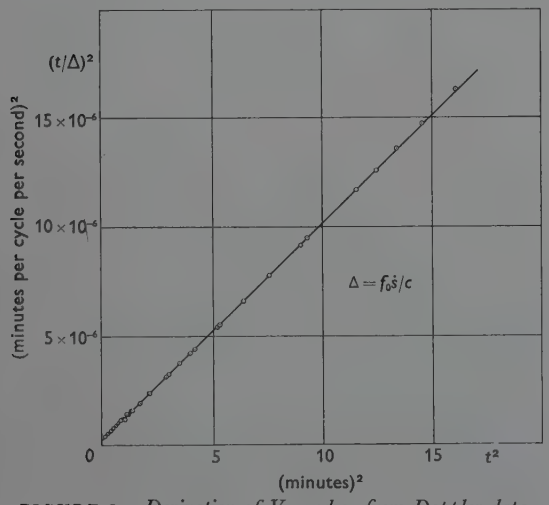


FIGURE 2 – *Derivation of V_R and s_0 from Doppler data.*

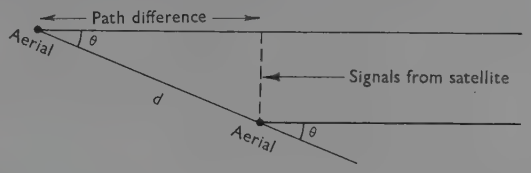


FIGURE 3 – *Principle of the interferometer.*

metres—is very small compared with the satellite's distance, so that the waves from the transmitter may be considered to traverse parallel paths (figure 3).

If the satellite happens to be at such an angle that the path difference is exactly equal to half a wavelength, i.e. if

$$d \cos \theta = \lambda/2$$

the combined output from the two aerials is zero, since the separate waves interfere completely. Evidently this will also occur whenever the path difference is equal to an odd number of half-wavelengths: as the satellite progresses along its orbit, the change in direction of the incoming radiation causes a succession of such zeros, the pattern depending on the direction of the track with respect to the line joining the aerials. During the interval between successive zeros the increase in $\cos \theta$ is λ/d, so that a record of the times at which the zeros occur gives immediately the rate of change of the direction cosine.

Instead of simply adding the signals at the two aerials it is preferable to measure their phase difference; in this way a continuous indication of $\cos \theta$ is available [2], and at the same time the measurement is almost independent of amplitude fluctuations.

Since the interferometer is insensitive to changes of a whole number of wavelengths in the path difference there are ambiguities in the measurement of the angle θ, which become more numerous as the aerial separation is increased. They can only be resolved from an approximate knowledge of the satellite's track obtained from another source, such as a second interferometer with a pair of aerials set much closer together, giving a 'coarse' and 'fine' indication. The 'fine' system obtained with the wider separation is of course more accurate, because a given electrical phase difference corresponds to a smaller increment in $\cos \theta$; but this cannot be carried too far, for the measurement of phase becomes more difficult as the separation is increased.

Another direction cosine can be derived from a similar set of aerials arranged at right angles to the first; it is then possible to define the direction of the line joining satellite and station during the

satellite's transit. To deduce the orbit, additional information is necessary, such as the distance and relative velocity supplied by the Doppler data, or the directions from other interferometers at different places. Failing this, some assumptions about the orbit must be made.

Radio techniques such as these have been found to give very useful orbital information; indeed, the orbit of the first Sputnik was established with fair accuracy by radio methods only [3, 4], in spite of the inconveniently low frequency of 40 Mc/s, while radio interferometry is the standard method for tracking the American satellites, equipped as they are with 108 Mc/s transmitters.

Unfortunately the radio methods require active assistance from the satellite: if the transmitter ceases to function, so too do the Doppler and interferometer stations. The transmitter of Sputnik 1 failed some three weeks after launch, while that of Sputnik 2 lasted less than a week. The advent of solar batteries, which store radiation from the sun as electrical energy, has greatly extended the natural life of such equipment, but the risk of mechanical or electrical failure is still present, and it is prudent to seek other methods to allow for this contingency.

RADAR TRACKING

One possibility is to place the transmitter on the ground and to use the satellite merely as a reflector of energy—the radar technique. The distance is great and the reflecting area small, so that a sufficiently strong echo is obtained only if the radiated power is concentrated in a narrow beam—which means a large aerial system and a small field of view. Thus, unless the orbit is known tolerably well, it is no easy matter to ensure that the beam is directed to the right part of the sky at the right time. The large radio-telescope at Jodrell Bank [5], among others [6], has been used in this role; the method has the twin advantages of independence of satellite-borne equipment and of local weather conditions—a combination enjoyed by neither radio nor visual methods.

OPTICAL TECHNIQUES

Optical observations, however, have played the major role in establishing accurate orbits for those satellites which have been visible. Both Sputnik 3 and its carrier rocket, for example, are easily detected by the naked eye, while to those who knew its habits Sputnik 2 became a familiar object during its six months' sojourn in the heavens. Many methods are used, ranging from naked-eye and stop-watch observations to refined telescopic and photographic techniques. The former are invaluable for prediction purposes, since no lengthy process of data reduction is involved; in this way it is possible to forecast with fair accuracy the satellite's expected position at future transits—a service which is of great help in preparing for observations with the more accurate instruments.

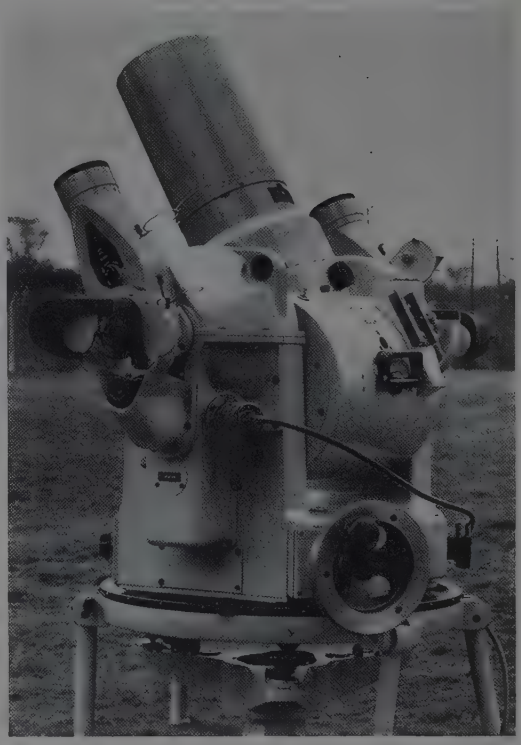


FIGURE 4 – *A kinetheodolite.*

Among the latter must be counted the kinetheodolite, which has given excellent results for the second and third Russian satellites. This optical instrument (figure 4) is controlled by two operators, one tracking in azimuth and the other in elevation. An internal flash-camera periodically photographs the scales, thus recording azimuth and elevation angles; at the same time the satellite is photographed through a long-focus lens mounted on the kinetheodolite. The purpose of the latter operation is to allow for errors in tracking: the displacement of the satellite's image on the photograph enables a correction to be made to the recorded azimuth and elevation angles. The exposures are controlled by accurate timing equipment at a rate of about five per second, so that during the course of a single transit some hundreds

of readings may be recorded. These instruments were used extensively at various Ministry of Supply stations to establish an accurate orbit for Sputnik 2; under good conditions an accuracy of 20 seconds of arc was achieved, with a timing error of less than 20 milliseconds.

All the methods which have been described yield the satellite's displacement or direction as seen from a point on the Earth's surface—usually one of the observing stations—and this point is rotating with the Earth. But the Earth's diurnal motion plays no part in the satellite's progress: this is determined by the gravitational attraction directed (to a first order) towards the centre of the Earth, so that the simplest description of the orbit is to be found in a non-rotating reference frame with origin at the Earth's centre.

The transfer of information from topocentric to geocentric co-ordinates is somewhat involved and is best handled by a digital computer, which can also be programmed to minimize the effects of random observational errors. A programme evolved by R. H. Merson [7] for this purpose makes light work of the calculation: from kine-theodolite data, for example, the machine computes the best estimates of the orbital elements—the size and shape of the ellipse (for the orbit is approximately elliptical) and its orientation in space.

ORBITAL PERTURBATIONS

The satellites now circling the Earth carry a comprehensive range of instruments to sample the various physical conditions obtaining in space, with arrangements for transmitting the data back to Earth. Compared with the spate of information collected in this way the contribution from tracking data appears very meagre. This would indeed be so were the Earth strictly spherical and without an atmosphere: there would then be little interest in deriving accurate orbits for satellites near to the Earth. Apart from very small perturbations due to the Sun and other bodies in the solar system, the path would be an ellipse with one focus at the Earth's centre (figure 5); moreover, the ellipse would maintain a constant orientation in space. However, the presence of the atmosphere and the slight flattening of the Earth's surface at the poles both induce deviations from this simple state of affairs—deviations which, if measured accurately enough, can shed light on the phenomena which produce them. It is fortunate that the effects on the orbit of atmospheric drag and of the Earth's oblateness are quite distinct (at least to a first order), so that each effect can be unambiguously referred to its cause.

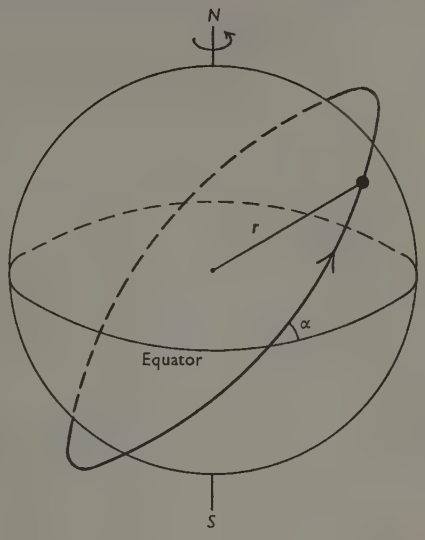


FIGURE 5 – *Inclination of the orbital plane.*

The non-uniform nature of the Earth's mass distribution results in a gravitational field which is not inversely proportional to the square of the radial distance. The external gravitational potential can be expressed as a series of spherical harmonics [8], the coefficients of each harmonic depending on the shape and mass distribution of the Earth; if then these coefficients can be determined, it is possible to deduce the figure of the Earth.

INFLUENCE OF THE EARTH'S OBLATENESS

The effects of such a non-central force on the orbit of a near Earth satellite has been studied theoretically [9], assuming the Earth to be an ellipsoid with a gravitational field which is independent of longitude and symmetrical about the equatorial plane. It is found that the orbital plane, instead of remaining in a fixed direction, rotates slowly about the Earth's axis. This precession, which is in a direction opposite to the satellite's motion, is of course quite distinct from the apparent precession observed from the Earth's surface, due to the rotation of the Earth. The expression for the rate of precession is rather lengthy, but to a good approximation it is

$$J\left(\sqrt{\frac{g}{R}}\right)\left(\frac{R}{\bar{r}}\right)^{3\cdot5}\cos\alpha$$

where g is the magnitude of the gravitational field at the equator, R the Earth's equatorial radius, $\bar{r}$ the harmonic mean distance of the satellite from the Earth's centre, and α the inclination of the

orbit to the equatorial plane. J is a coefficient associated with the second harmonic in the gravitational expansion, and is a measure of the Earth's oblateness.

A secular variation also occurs in the orientation of the ellipse in the orbital plane; the major axis rotates at a rate given by

$$\frac{J}{2}\left(\sqrt{\frac{g}{R}}\right)\left(\frac{R}{\bar{r}}\right)^{3\cdot5}(5\cos^2\alpha - 1)$$

The rate of rotation thus depends on the orbital inclination: it is in the same direction as the satellite's motion if α is less than 63·4°, and in the opposite direction for larger angles.

Apart from the secular effects, there are periodic departures from the ellipse. The largest of these disturbances has a period equal to half the orbital period of the satellite, and an amplitude

$$\frac{JR^3}{6\bar{r}}\sin^2\alpha$$

The first three Russian satellites all had an orbital inclination near 65°, so that the rotation of the major axis was very slow and difficult to measure, while the periodic changes in radial distance amounted to only one or two kilometres. The mean rate of rotation of the orbital plane, however, can be found accurately from observations over a long period, and offers the best hope of correlating theory and observation.

The theoretical and observed rates of precession for Sputnik 2 are compared in figure 6. The broken line is derived from theory, using the measured values of $\bar{r}$ and α and the accepted values for the geophysical constants. Both curves are subject to error—the first in the measured value of α and $\bar{r}$, and the second in the observed rate; but it turns out that the difference evident in the figure is significant. The observed rate suggests a lower value than is currently accepted for the ellipticity of the Earth.

However, the discrepancy may be due to other factors, such as atmospheric drag or asymmetry in the gravitational field. These effects have not yet been worked out in detail, but it is evident that, by accurately tracking satellites at different inclinations, it may be possible to improve our knowledge of the shape of the Earth, and as a consequence to define distances between points on its surface more precisely.

ATMOSPHERIC EFFECTS

The non-central gravitational field does not alter the general shape of the ellipse, apart from producing the small radial perturbation, but

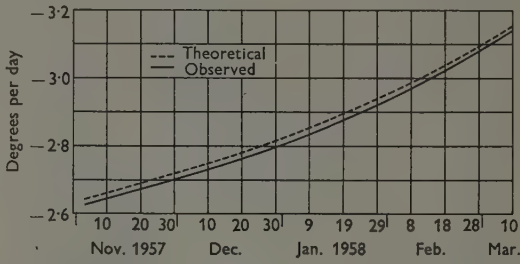


FIGURE 6 – *Rate of rotation of orbital plane of Sputnik 2.*

merely its orientation in space; the eccentricity and major axis are not affected, the perigee and apogee remaining at constant distances from the Earth's centre. The effect of the atmosphere is precisely the opposite: the major contribution of air drag is to distort the ellipse, with very little influence either on the rotation of the orbital plane or on the orientation of the ellipse in that plane.

For an eccentric orbit the retardation due to atmospheric drag varies during one revolution. The perigee heights of the first three Russian satellites were all in the region of 225 km, with apogees ranging from 900 km to 1900 km; and, since the air density falls away exponentially with height, the drag at perigee was enormously greater than at apogee for these satellites. The retardation at perigee causes a loss of height at the subsequent apogee; the orbit thus becomes less eccentric, but with very little change in perigee height. When the orbit has become circular, or almost so, the drag is more nearly constant, so that rather different conditions obtain: the satellite begins to descend in a spiral path, slowly at first, and then at an increasing rate until it is burnt up in the lower atmosphere.

The outward signs of these phenomena are a decrease in the orbital period and an increase in the satellite's speed—at first glance a puzzling feature, until it is remembered that the satellite

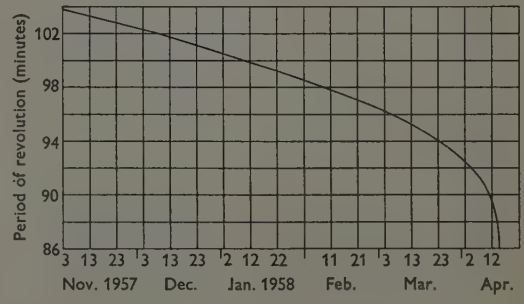


FIGURE 7 – *Period of revolution of Sputnik 2.*

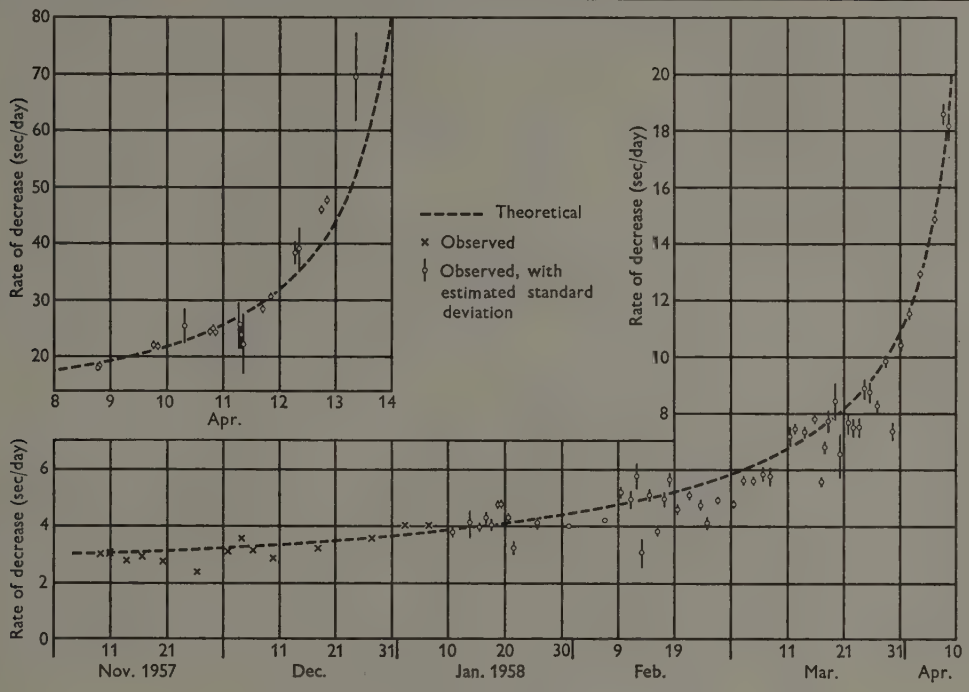


FIGURE 8 – *Rate of change of period of Sputnik 2.*

suffers a loss in height, and therefore in potential energy. This loss more than balances the increase in kinetic energy, so that there is a net loss of energy—that which is expended in overcoming air resistance.

The change in orbital period during the lifetime of Sputnik 2 is shown in figure 7; the period decreases at an increasing rate because of the greater air resistance at the lower altitude. It is evident that the rate of decrease is related to the air drag, which in turn depends on the density of the air and on the shape, size, and mass of the satellite.

The relationship is simply derived for a circular orbit. Since the gravitational intensity at a distance r from the centre of the Earth (considered uniform and spherical with radius R) is gR^2/r^2, the velocity v appropriate to a circular orbit at that distance is given by

$$\frac{v^2}{r}=\frac{gR^2}{r^2}$$

so that if the height decreases by a small amount Δr during one revolution, the gain in kinetic energy is

$$\tfrac{1}{2}mgR^2\left(\frac{1}{r+\Delta r}-\frac{1}{r}\right)\doteq\tfrac{1}{2}mv^2\frac{\Delta r}{r}$$

where m is the mass of the satellite. The loss of potential energy is

$$m\,.\,g\frac{R^2}{r^2}\,.\,\Delta r=mv^2\frac{\Delta r}{r}$$

which is precisely twice the gain in kinetic energy. The difference between these must equal the work done against the drag force F during one revolution:

$$\tfrac{1}{2}mv^2\frac{\Delta r}{r}=2\pi rF$$

The drag F may be written as

$$F=\tfrac{1}{2}\rho v^2SC_D$$

where ρ is the air density, S the area normal to the path, and C_D the drag coefficient. Thus

$$\frac{\Delta r}{r}=2\pi r\rho\frac{SC_D}{m}$$

The change in radius may be expressed in terms of the decrease in orbital period T by observing that

$$T=\frac{2\pi r}{v}=\frac{2\pi}{R\sqrt{g}}\,.\,r^{3/2}$$

from which

$$\frac{\Delta r}{r}=\tfrac{2}{3}\frac{\Delta T}{T}$$

The fractional change in orbital period can be measured very accurately, so that if SC_D/m is

known it is possible to derive the density ρ at the height $r-R$.

The analysis can be extended to include non-circular orbits [10], giving in principle a continuous measure of air density; but for any shape other than a sphere it is difficult to estimate the effective area S, because of the changing attitude. At these very low densities there is virtually no aerodynamic damping, so pitching, yawing, and rolling motions, once acquired, tend to persist. The erratic behaviour of the orbital period is well illustrated in figure 8, which shows the rate of change of period for Sputnik 2. This satellite was roughly cylindrical, and the marked changes in brightness noted on most transits suggest that variations in orientation did in fact occur. The irregularity in period may of course partly reflect fluctuations in atmospheric density; but other disturbances—magnetic or electrostatic forces, for example, or meteoric bombardment—cannot be discounted, and systematic observations on many satellites are necessary if the phenomenon is to be fully explained.

The cumulative effect of air resistance eventually leads to the demise of a satellite. Its lifetime can be estimated from the change in orbital period [10], although the prediction is again somewhat uncertain, for the reasons just given.

IONOSPHERIC PHENOMENA

The propagation of electromagnetic waves in the ionosphere furnishes another area of investigation for which orbital data are highly desirable. Considerable attention has been devoted to ionospheric phenomena, but not until the launching of the first Earth satellite was it possible to study the transmission of waves from outside or within the ionized layers. A large store of data now exists and awaits analysis, but it is already evident that the paths by which signals are received may be extremely complicated. The value of such radio data is greatly enhanced if the location of the source with respect to the observing stations is accurately known, for then a comparison of the true direction with the apparent direction given by the radio signals indicates the amount by which the radio path is bent by the ionosphere. The bending will depend on the frequency used and on the angle of elevation, being least for overhead transits and greatest for low elevations. A series of radio observations of different frequencies and elevations, together with the true directions, should yield valuable information on the structure of the ionosphere.

Simultaneous radio and optical observations from the same station would be ideal for this purpose, but failing this it should be possible to establish the optical path sufficiently well from an accurately determined orbit.

CONCLUSION

The various tracking methods which have been touched upon are complementary rather than competitive. Each method has its advantages—the all-round view of the radio methods, the self-sufficiency of the radar system and its indifference to cloud cover, the immunity of optical observations from the vagaries of the ionosphere—and all are necessary to provide a clear picture of the satellite's behaviour and to further the study of the Earth and its environs.

Observations from one country, however, are most efficiently used in combination with similar data from other countries. In this connection the World Data Centres, set up by a special committee of the International Council of Scientific Unions to operate during the International Geophysical Year, should prove of great value; their functions are broadly to accept information from a multitude of observers, to analyse it, and to disseminate their results. Fortunately a satellite, whatever its country of origin, is freely available for tracking purposes, and, appropriately, the knowledge gained from a study of its orbit is of global interest.

ACKNOWLEDGMENTS

I am very grateful to my colleagues, Mr A. N. Beresford and Mr W. T. Blackband, who have provided much of the material concerning radio methods; and to Mr D. G. King-Hele and Mr R. H. Merson for their work on orbital perturbations in theory and practice.

REFERENCES

[1] HAMPTON, D. E. *Proc. Instn Elec. Engrs, B*, **105**, 99, 1958.
[2] BERESFORD, A. N. *Ibid., B*, **105**, 85, 1958.
[3] Staff of the Mullard Radio Astronomy Observatory, Cambridge. *Nature, Lond.*, **180**, 879, 1957.
[4] Staff of the Royal Aircraft Establishment, Farnborough. *Ibid.*, **180**, 937, 1957.
[5] DAVIS, J., EVANS, J. V., EVANS, S., GREENHOW, J. S., and HALL, J. E. *Proc. Instn Elec. Engrs, B*, **105**, 105, 1958.
[6] HEY, J. S. *Ibid., B*, **105**, 107, 1958.
[7] KING-HELE, D. G. and MERSON, R. H. *J. Brit. Interplan. Soc.*, 1958. (In press.)
[8] JEFFREYS, H. 'The Earth' (third edition), Ch. 4. Cambridge University Press, London. 1952.
[9] KING-HELE, D. G. *Proc. roy. Soc.*, 1958. (In press.)
[10] KING-HELE, D. G. and LESLIE, D. C. M. *Nature, Lond.*, **181**, 1761, 1958.

Book reviews

WHITE DWARF STARS

White Dwarfs, *by E. Schatzman. Pp. viii + 180. North-Holland Publishing Co., Amsterdam.* 1958. *Fl.* 19 *net.*

The interesting class of stars known as 'white dwarfs' consists of stars of very low intrinsic luminosity, fairly high surface temperature, very small size, and extremely high mean density. Because of their low luminosity, all the known white dwarfs (about 250 in number) are relatively near stars, but the distances of only 30 have been determined with precision.

The great interest of the white dwarfs lies in the fact that the material of which the star is composed does not obey the perfect gas laws because of its very high density. It is known as degenerate matter. This gives rise to many problems of great theoretical interest, which are fully dealt with in this monograph. The treatment is necessarily highly mathematical.

It appears that hydrogen cannot exist, and helium content must be very low, in the interior of a white dwarf. The internal core consists almost entirely of heavy elements, with a thin outer envelope, probably of almost pure hydrogen. The energy generated by thermonuclear reactions must be very small. Vibrational instability may result from the generation of energy by the hydrogen cycle in the envelope of the star and may give rise to recurrent explosions accompanied by the ejection of thin gaseous shells. The lifetime of a white dwarf is, however, very long, of the order of 10^{11} years.

The origin of white dwarfs is uncertain. Stars of mass much greater than that of the Sun could become white dwarfs only after losing much of their mass. It is possible that some white dwarfs have evolved from novae that have undergone a great number of recurrent outbursts. It is very improbable that the white dwarf stage is a normal product of stellar evolution. A number of binary and multiple stars contain a white dwarf in association with one or more normal stars, and white dwarfs are present in some relatively young clusters of stars.

The available information about the white dwarfs, both observational and theoretical, is summarized and discussed in this monograph, from which it is clear how incomplete is our present knowledge and understanding of their nature and evolution. It contains many minor errors and misprints which could have been avoided by more careful proof reading. H. SPENCER JONES

RADIO ASTRONOMY

The Exploration of Space by Radio *by R. Hanbury Brown and A. C. B. Lovell. Pp. xii+207. Chapman and Hall Ltd, London.* 1957. 35*s. net.*

Professor Lovell is the director of the Jodrell Bank Experimental Station and has been largely responsible for the successful completion of the giant 250 foot radio telescope which is just being brought into operation. In writing this book he and Hanbury Brown have presumably had in mind the provision of an up to date background knowledge of radio astronomy against which the future programme of the telescope can be seen in perspective. Such a volume is the more welcome because of the rapid progress of the science and the fact that the only other comprehensive text, 'Radio Astronomy,' by J. L. Pawsey and R. N. Bracewell, includes no work published since 1952.

The eleven chapters deal with the astronomical background; some properties of radio waves; techniques of radio astronomy; galactic and extragalactic radio emissions; the hydrogen line; the scintillation of radio stars; solar radio waves; meteors; radio and the aurora borealis; radio investigations of the moon, planets and the earth satellites; and the Jodrell Bank radio telescope. Not unnaturally those aspects of the subject which have been the particular concern of the Manchester teams, e.g. meteors, have had special emphasis.

This is not a book for the layman and a knowledge of some physics is essential for its understanding. More references would have been desirable and explanations about such techniques as 'post-detector correlation' should have been either fuller or not attempted. Occasionally concepts such as 'optical depth' are introduced without comment, but despite the necessary condensation it is, on the whole, a lucid account of radio astronomy.

The book is well printed and free from serious errors, apart from an unfortunate diagram in Figure 33. There are 27 plates, 10 of which illustrate the Jodrell Bank telescope.

J. R. SHAKESHAFT

MOLECULAR PHYSICS

Molecular Physics. *Vol. I, No. 1, pp.* 98. *Taylor and Francis Ltd, London.* 1958. 25*s. per part; £4* 15*s. subscription per volume.*

'Molecular Physics' is a new international journal intended to bring together papers on all aspects of the physics of molecules from all parts of the world. The truly international character is emphasized by the form of the Editorial Board which includes representatives of twelve countries; the languages used will be English, French, or German.

The first issue, dated January 1958, sets a very high standard. It includes contributions on nuclear magnetic resonance, dipole moments, rotational spectra, and critical opalescence in solid solutions. In addition there are a number of theoretical papers on electron distribution in molecular hydrogen, on the application of Prigogine's general theory of irreversible processes to quantum-mechanical systems, and on statistical mechanics.

The quality of the presentation and printing is excellent. R. E. RICHARDS

ATOMIC HYDROGEN SPECTRUM

The Spectrum of Atomic Hydrogen, *by G. W. Series. Pp. viii + 88. Oxford University Press, London.* 1957. 8*s.* 6*d. net.*

Throughout the history of quantum theory the hydrogen atom and its spectrum have played a major role. At each stage in the development of the theory applications were made to hydrogen, discrepancies between theory and experiment became apparent, and further theoretical development followed. This book gives a clear account of the successive theories and of the comparison of each theory with contemporary experimental knowledge. The book should be considered as a supplement to, rather than a substitute for, existing textbooks on quantum mechanics.

Of wider interest are the chapters on the experiments of Lamb and Rutherford and on the New Quantum Electrodynamics. These deserve to be read by the many scientists who have been unable to keep abreast of modern developments described in the periodical literature.

The title of the book is misleading in that students reading the book will get a rather one-sided view of the importance of the spectrum of atomic hydrogen in modern scientific research.

Astrophysical aspects of the subject are not mentioned; the detection and interpretation of radio-frequency line radiation of cosmic atomic hydrogen is an outstanding achievement.

The publishers are to be commended on producing this excellent book at such a reasonable price. R. H. GARSTANG

NUCLEAR SCIENCE

Annual Review of Nuclear Science. *Vol. VII, edited by J. G. Beckerley. Pp. v + 496. Annual Reviews Inc., California.* 1957. $7 *net.*

This volume continues the editorial policy set out four years ago of informing specialists in one field about the situation in another, on the assumption that the specialist is willing 'to prepare himself with a minimum knowledge of the fundamentals of the new field.' This specialist, having enjoyed a splendid, though in places very theoretical, account of elementary particles, turned hopefully to Vertebrate Radiobiology (Lethal Actions and Associated Effects), only to find that physics and a social conscience could not get him beyond the first page. The minimum knowledge of fundamentals clearly extended well beyond a pass at Second M.B.

What then is the real purpose of this series as opposed to its avowed one? The paradoxical answer is that its greatest success lies in bringing the specialist up to date in his own field by slightly extending his horizon to include at least parts of the fields of his neighbours. Thus I found myself thoroughly at home with one article, profited greatly from two, exhibited an intelligent interest in three more—all six clearly excellent articles—but did not get beyond the first paragraph of the other six. This may be a respectable score, but are money and shelf space so plentiful that one can afford to buy so much that one can never hope to understand and that will be outdated in a very few years? L. R. B. ELTON

CRYSTAL PHYSICS

Experimental Crystal Physics *by W. A. Wooster. Pp. viii + 115. Clarendon Press, Oxford.* 1957. 18*s. net.*

Most books on the physical properties of crystals deal mainly with theory. This one, which is based on the course that has grown up in the Department of Mineralogy and Petrology in Cambridge, is concerned with laboratory work. The experiments are designed to illustrate principles rather than to achieve high accuracy, and are limited by the practical considerations that suitable crystals should be readily obtainable and the exercise should be capable of performance in an hour or two. A brief general discussion of each topic is followed by details of the apparatus and examples are given showing how the desired quantity is calculated. The largest section is devoted to optical constants of transparent and opaque substances. Dia-magnetic and para-magnetic properties, thermal conductivity and thermal expansion, piezo-electricity, pyro-electricity, and elasticity, are included by measurements of constants or qualitative demonstrations as appropriate. It is a very practical introduction to the subject.

H. M. POWELL

CATALYSIS

Contact Catalysis (*third edition*), *by R. H. Griffith and J. D. F. Marsh. Pp. x + 299. Oxford University Press, London.* 1957. 50*s. net.*

This, the third edition, re-written and enlarged, of Griffith's 'The Mechanism of Contact Catalysis,' presents in moderate compass a very large amount of factual information on adsorption and contact catalysis, and also outlines most of the modern theories, including the importance of lattice defects, the electronic factor emphasized by Dowden, and geometrical correspondence between adsorbed molecules and catalyst surface. There is also much practical information on the preparation of catalysts. The bibliography is excellent and the reader should have no difficulty in following up any theoretical or practical topic.

While the book is a mine of information, it is not easy to read consecutively, for it is largely a series of abstracts of experimental and theoretical papers. The argument is often condensed and does not flow smoothly from one section to the next, and the arrangement seems a bit hasty, with some overlapping between chapters. Correction of parts perhaps dictated is skimped in places: Tompkins appears as Tomkins and Wahba as Wobba! But some integration has been achieved and many suggestions for further work are made. The book is probably the best broad, as well as detailed, survey of this extremely complex field yet published, and should be invaluable to both academic and industrial chemists.

The authors' concluding remarks that 'the broad outlines of the subject are becoming clear,' even though 'the detailed mechanisms of individual reactions have rarely, if ever, been elucidated,' are probably justified.

N. K. ADAM

QUANTITATIVE INORGANIC ANALYSIS

Quantitative Inorganic Analysis, *by G. Charlot and Denise Bézier. Translated from the third French edition by R. C. Murray. Pp. x + 691. Methuen & Co. Ltd., London; John Wiley & Sons Inc., New York.* 1957. 84*s. net.*

Charlot and Bézier broke fresh ground when their book first appeared in 1944. In the revised third French edition (from which this translation has been made) they attempt a general survey of all the methods used in quantitative analysis. In the first part (322 pages) they deal with the various approaches, emphasizing different types of reactions and the fundamental theoretical principles. In the second part (316 pages) the determination of each element is considered in turn, a deliberate and critical choice of methods being attempted rather than a complete coverage. The last 46 pages include numerical data, bibliographies, and indexes.

The authors have, deliberately, not attempted to rival existing text-books which set out detailed procedures for quantitative determinations. It is a pity that, while they present a rich mine of information on other aspects of analysis, often in a novel and always in an interesting way, the treatment inevitably lacks detail and sometimes balance. Thus chromatography in all its aspects is dismissed in seven pages, emission spectrography and the uses of radioactivity each secures five pages, the determination of traces only three, and sampling only one page. The staccato style of the original must have been troublesome to translate and explains the occasional infelicity and inaccuracy.

Despite its weaknesses, this is a book to interest and stimulate all teachers and students and admirably suited to show the wide range and variety to be found in the continually expanding field of modern quantitative analysis.

H. IRVING

OXIDATION-REDUCTION TITRATIONS

Volumetric Analysis. *Vol. III*—Titration Methods: Oxidation-Reduction Reactions, *by I. M. Kolthoff and R. Belcher with the co-operation of V. A. Stenger and G. Matsuyama. Pp. ix + 714.*

Interscience Publishers Inc., New York; Interscience Publishers Ltd, London. 1957. $15 *net.*

With the publication of volume III the treatise on Volumetric Analysis begun in 1942 by Professor Kolthoff is complete. The first volume dealt with theoretical fundamentals; volume II published in 1947 covered acid-base, precipitation, and complex-formation reactions. The present volume is devoted wholly to oxidation-reduction reactions.

The collective authorship to which Professor Kolthoff draws attention in his preface is a result of the withdrawal first of Dr Stenger, his collaborator in the two earlier volumes, and then of Dr Matsuyama. The work was finally completed with the help of Dr Belcher.

After a general introductory chapter there follow chapters on permanganate, ceric sulphate, potassium dichromate, iodometry applied both to inorganic and organic determinations, the Karl Fischer determination, potassium iodate, periodate, potassium bromate, and the hypohalites. The last two of the fifteen chapters deal with a number of strong reducing agents, (i.e. ferrous, titanous, stannous, mercurous, vanadous, and chromous salts), and with a miscellaneous collection of oxidizing and reducing titrants.

It is impossible in a short review to indicate in more detail the scope of this work but it will be appreciated that in a book of over 700 pages devoted solely to titrations based on oxidation-reduction reactions a most comprehensive coverage has been achieved. This volume will worthily command a place beside those earlier 'Kolthoff's on the analyst's shelves. The printing and binding are excellent.

R. C. CHIRNSIDE

QUANTITATIVE ORGANIC ANALYSIS

Quantitative Organic Analysis, *by J. S. Fritz and G. S. Hammond. Pp. ix + 303. John Wiley & Sons Inc., New York. Chapman and Hall Ltd, London.* 1957. 52*s. net.*

Comparatively few organic reactions proceed quantitatively and chemists are frequently faced with the problem of analysing mixtures of products. The present volume describes methods based upon selective functional-group reactions whereby individual components can often be estimated without the necessity of first isolating them. Most of these methods are quite new and the authors themselves have made many contributions to the subject.

Apart from chapter 2, which is rather heavy going, the text is written clearly and is enjoyable to read. A particularly valuable feature is the stress laid on the reasoning leading to a particular choice of method and to the way in which existing methods can be adapted or new methods devised to solve new problems. Indeed a whole chapter is devoted to the latter aspect. Other chapters deal with methods involving acid-base titrations in non-aqueous solvents, redox reactions, spectrophotometry measurement of physical properties, metal ion complexes, kinetics in analysis, separations and elemental analysis. Some detailed examples of procedures are given at the end.

Although primarily intended for teaching purposes in the United States, in Britain this book will find its greatest use among research workers and all professional analysts who wish to apply up-to-date methods to their problems.

JOHN F. W. McOMIE

ORGANIC SYNTHESES

Organic Syntheses, *vol. XXXVII, edited by J. Cason. Pp. vii + 109. John Wiley & Sons Inc., New York; Chapman and Hall Ltd, London.* 1957. 32*s. net.*

This latest volume of the annual series which started as early as 1921 contains detailed instructions for the preparation of 31 organic compounds. These include benzfurazan oxide, benzoylacetanilide, 3-benzoylpyridine, 2-chloronicotinonitrile, diaminouracil hydrochloride, *trans*-2-dodecenoic acid, ethyl α-nitrobutyrate, *n*-heptamide, parabanic acid, and *ar*-tetrahydro-α-naphthol. The most novel syntheses are the preparation of norbornylene in up to 71 per cent yield from di*cyclo*pentadiene and ethylene, and of pseudopelletierine from 2-ethoxy-3:4-dihydro-2H-pyran by hydrolysis to glutaric dialdehyde and condensation with methylamine and acetone dicarboxylic acid.

The reviewer has long felt that the usefulness of these volumes would be enhanced by the addition to the accounts of certain of the preparations of a few words and references as to their synthetical potentialities. This is hardly necessary for compounds which are obviously general intermediates or starting points for a wide variety of synthesis, such as diethyl benzoylmalonate, ethyl benzoylacetate, glutaric acid and imide, oleoyl chloride, or stearolic acid, all of which are described in the present volume. On the other hand, it would clearly be of interest to have such notes on e.g. 2-chloro-2-methyl*cyclo*hexanone, 1-diethylamino-3-butanone, 3:4-dinitro-3-hexene, 1:4-diphenyl-5-amino-1:2:3-triazole, 4-ethyl-2-methyl-2-octenoic acid, ethyl *tert.*-butyl malonate, isophorone oxide, and trichloromethylphosphoryl dichloride, the preparations of which are also included in the volume under review.

W. BAKER

ORGANOMETALLIC COMPOUNDS

The Chemistry of Organometallic Compounds, *by E. G. Rochow, D. T. Hurd, and R. N. Lewis. Pp. vi + 344. John Wiley & Sons Inc., New York; Chapman and Hall Ltd, London.* 1957. 68*s. net.*

There is a wide interest in organometallic compounds and this excellent book by well-known workers in this field of chemistry will be assured of a warm welcome. The authors state that they have tried to present the theoretical, factual, and practical aspects of organometallic compounds in a form which will be useful to the student and to the more general reader with a background of elementary chemistry. Obviously the authors have had to be selective in deciding upon subject-matter but in the opinion of the reviewer they have produced a volume that will be found of real value both to students and to research workers who may contemplate entering this field of investigation.

The book opens with an account of the general physical and chemical properties of organometallic compounds, and this is followed by a discussion of the general properties of the carbon-metal bond. The third chapter deals with the various methods which are available for the preparation of organometallic compounds. Against this background the authors systematically survey the compounds formed with the metallic and metalloidal elements. Of particular interest here are the organometallic compounds of the transition metals. (In 1951 the discovery of the *cyclo*pentadienyl compounds of iron excited great interest and opened up investigations which have resulted in an extensive organometallic chemistry of almost all the transition metals and most of the rare earths.) A very interesting chapter deals with applications of organometallic compounds in organic synthesis and in the section concerned with the simple olefines a discussion of the Ziegler process is

included. The final chapter is devoted to an account of special types of organometallic compounds such as the fluorocarbon derivatives, olefine complexes, carbonyl compounds, cyanide and *iso*nitrile complexes and carbides. Although the hydrides fall outside the definition of organometallic compounds the authors mention them as they consider that a comparison of the metal hydrides with the corresponding organometallic compounds discloses some interesting features. With only a few exceptions organometallic compounds require special techniques for their preparation, purification, and handling. A detailed account of such experimental methods is not included in this volume but a short section entitled 'materials-handling techniques' contains some excellent advice. However, the novel method suggested for the disposal of highly volatile materials has obvious limitations. The text is liberally augmented with references to the chemical literature. The authors can be congratulated on achieving the aims they set themselves and producing a volume which looks well, reads well, and cannot fail to stimulate increased interest in this special field of chemistry.

W. WARDLAW

CLIMATOLOGY

Climatology (*second edition*), *by W. G. Kendrew. Pp. xv* + 400. *Clarendon Press, Oxford.* 1957. 42*s. net.*

The second edition of this well-known textbook incorporates many minor changes as well as some new sections on such subjects as jet streams and blocking anticyclones, all of which serve to bring the work up to date. The added index of place names will prove useful, but the index of subjects is still somewhat inadequate.

In the preface the author states that considerations of space exclude details 'such as the periods for which the mean values of climatological data used in the book are computed.' An omission such as that specified can hardly be justified by describing it as 'a point of subsidiary importance'; for unless the period covered by some mean value is stated, such a value has much less significance than is sometimes attributed to it. In particular, a comparison of mean values for different stations, which some of the graphs and tables invite, is certainly not justified unless such values cover the same period.

A few errors still remain, e.g. on page 71 the 'Mean monthly min.' temperature for July at Léopoldville and Kabete is in each case shown to be 1° lower than the 'Abs. extreme min.' However, this excellent introduction to modern climatology is much more than a mere collection of dull facts. It brings climatology to life, and it should certainly be possessed by every student of the subject.

F. G. HANNELL

CELL STRUCTURE

Macromolecules in Cell Structure, *by A. Frey-Wyssling. Pp. vii* + 112. *Harvard University Press, Cambridge, Mass.; Oxford University Press, London.* 1957. 40*s. net.*

The gap between the cell physiologist and biochemist on the one side and the morphologist on the other was wide and long unbridged. A substantial bridge has now been built with the aid of modern physical techniques such as X-ray diffraction and electron microscopy. In this building, none has been more active than Professor A. Frey-Wyssling. Frey-Wyssling was in this field before techniques were developed to their present stage and has used them with skill to test his own earlier hypotheses of structure at the submicroscopic level.

This book, based on the Prather Lectures delivered at Harvard University in 1956, traces briefly the development of the author's ideas, and supplements the longer account published in 1953 in his authoritative book, 'Submicroscopic Structure of the Cytoplasm.' Most of the examples are drawn from plants, largely from the work of the author or his colleagues in Zurich. Chapters on the fine structure of starch grains and of cell walls are followed by discussion of growth and differentiation in cell walls. The structure of chloroplasts and macromolecules in the cytoplasm are the last of two lectures in an interesting, well-illustrated, and readable book.

R. N. ROBERTSON

PROGRESS IN ENZYMOLOGY

Advances in Enzymology and Related Subjects of Biochemistry, *Vol. XIX, edited by F. F. Nord. Pp.* 457. *Interscience Publishers Inc., New York; Interscience Publishers Ltd, London.* 1957. $9.85 *net.*

This volume of Advances in Enzymology contains five authoritative reviews of exceptionally high standard. Vishniac, Horecker, and Ochoa describe various enzyme systems involved in metabolic pathways in photosynthetic cells under the heading 'Enzymic Aspects of Photosynthesis.' H. S. Mason's article on the mechanisms of oxygen metabolism is a comprehensive monograph of over 150 pages citing 842 references. The chemical mechanisms of three types of enzyme-catalysed oxidation reaction are described, oxygen transfer, electron transfer, and mixed function oxidases. The author is clearly more expert on oxygen transfer and mixed function oxidases than on electron transfer and the latter is treated only briefly. Wieland and Pfleiderer in an article *Aktivierung von Aminosäuren* give a very good account of the mechanisms of reactions of the type which are likely to be involved in the formation of peptide bonds during the biosynthesis of proteins. Kimmel and Smith in a review of the properties of papain describe a subject which is almost entirely their own. It is a nice object lesson of how the study of the physical and chemical properties as well as of the reaction mechanism of an isolated enzyme should be developed. The final article by Braunstein on *Les voies principales de l'assimilation et dissimilation de l'azote chez les animaux* presents a very scholarly review of up to date ideas on nitrogen metabolism. This is altogether a most valuable volume.

H. GUTFREUND

MARINE ALGAE

Marine Algae of the Northeastern Coast of North America (*second revised edition*), *by W. R. Taylor. Pp. viii* + 509. *The University of Michigan Press, Ann Arbor.* 1957. $12.50 *net.*

The first edition of this work appeared in 1937 and was the only complete account of the marine algae found along the North American Atlantic seaboard from Virginia to the Arctic Circle. In the intervening years it has come to be regarded as a classic in the phycological literature. This revised edition contains descriptions of more than 500 different marine plants found in the littoral and sublittoral zones, including a number of recently discovered species. The text has also been broadened to cover the results of current research on taxonomy and nomenclature.

Professor Taylor gives a history of the earlier work in this region, descriptions of the changes in the algal flora from one latitude to another, and directions for collection and preservation. Keys for orders, families, genera, and species are included in the descriptive catalogue. An excellent bibliography, covering 18 pages, is also included.

F. N. WOODWARD

Short notices of books

(These notices are descriptive rather than critical and are designed to give a general indication of the nature and scope of the books.)

Daedalus, *edited by P. Rieff. Pp.* 140, *American Academy of Arts and Sciences. Quarterly, subscription* $6.50 *per annum.*

The winter, 1958, issue of this journal is Volume 87, No. 1 of the Proceedings of the American Academy of Arts and Sciences, but is, in fact, the first issue in a new format. This issue is a special one devoted to 'Science and the Modern World View', and it, and subsequent issues are intended to link various sections of the academic world, and are directed at the educated public.

Atlas of the Sky, *by V. de Callatayï. Pp.* 157. *Macmillan & Co. Ltd, London; St Martin's Press, New York.* 1958. 65*s. net.*

Sir Harold Spencer Jones has translated this book from the French, and written a preface. The book is intended to enable the amateur astronomer, working without a telescope, to recognize the constellations and stars he can see. The illustrations include a number of plates which are representations of the sky in which the stars are depicted as white spots, graded according to their apparent brightness, on a black background, as well as many line drawings. There is also a text giving an elementary outline of modern astronomy.

Nuclear Radiation Detection, *by W. J. Price. Pp. vii*+382. *McGraw-Hill Book Co. Inc., New York and London.* 1958. 70*s. net.*

The intention of this book is to collect the basic information on all the important nuclear radiation detectors in use today; specific information on the application of the various detectors is given, to enable the reader to select and, often, to apply the equipment. While practically all the equipment described is available commercially, emphasis is given to the principles involved, with a view to making the book useful to the reader who desires to design his own equipment.

The Scaling-up of Chemical Plant and Processes, *edited by B. J. M. Pirie. Pp.* 136. *The Institution of Chemical Engineers, London.* 1958. £3 *net post free* (£2 *net post free to members of sponsoring bodies*).

This is the proceedings of a joint symposium that was held in London in 1957 and sponsored by the chemical engineering group of the Koninklijk Instituut van Ingenieurs, the chemical technology section of the Koninklijke Nederlandse Chemische Vereniging, and the Institution of Chemical Engineers. The subject is considered both generally and in detail, with a total of thirteen papers dealing with, amongst other things, the use of kinetics, the economic aspects, and with the scaling-up of particular pieces of apparatus, such as stirred slurry reactors, solvent extraction plant, gas absorption apparatus, and continuous filtration equipment.

Phenolic Resin Chemistry, *by N. J. L. Megson. Pp. vii*+323. *Butterworth's Scientific Publications, London; Academic Press, Inc., New York.* 1958. 65*s. net.*

The field covered in this book is that of the pure chemistry, as opposed to the technology, of the phenolic resins, mainly limited to those involving formaldehyde, and referring in detail only to developments since 1939. There are chapters on the phenolic alcohols, the ammoniacal and related phenol formaldehyde condensations, rational syntheses, and rates of reaction, amongst others. The author's aim has been to make a detailed survey and the range of references is very wide, including those in not widely understood languages, such as Japanese.

Population Studies: Animal Ecology and Demography. *Pp. xiv*+437. *Biological Laboratory, Cold Spring Harbor, New York.* 1957. $8 *net.*

This is volume XXII of the series of Proceedings of the Cold Spring Harbor Symposia on Quantitative Biology. Apart from introductory and closing speeches, there are 33 papers published here on the historical study of human populations, demographic theory, the experimental and theoretical study of animal populations, and other subjects connected with communities and populations. The papers include bibliographies.

Leptospirosis in Man and Animals, *by J. M. Alston and J. C. Broom. Pp. xii*+367. *E. & S. Livingstone Ltd, Edinburgh and London.* 1958. 40*s. net.*

The authors of this book aim at giving a survey of what is at present known about the leptospires and the diseases they cause in man and animals, and of the probable lines of future research; attention is given to the increasing frequency with which the disease occurs in some places, and the new serotypes involved. A chapter on the legal aspects of leptospirosis, by C. J. A. Doughty, has been added to make the survey comprehensive.

Scientific Glassblowing, *by E. L. Wheeler. Pp. xxii*+478. *Interscience Publishers Inc., New York; Interscience Publishers Ltd, London.* 1958. $9.75 *net.*

The modern glassblower can well be an understanding co-worker with the research chemist, and this book is designed to instruct the professional glassblower so that he may attain this level. It is written by a professional, and describes the cross-fire technique as used in America, giving instructions that start from simple joins and end with complicated vacuum and distillation apparatus. The book also has chapters on modern techniques, such as chromatography and distillation, that the author considers to be necessary background knowledge for the professional glassblower.

Immunology, *Vol.* 1, *No.* 1, *edited by J. R. Marrack. Pp. iii*+87. *Published quarterly by Blackwell Scientific Publications, Oxford.* 1958. 18*s. net per copy. Subscription* 60*s. per annum.*

This is the official journal of the British Society for Immunology, and this number contains eight papers on subjects related to immunity—three on skin homografts and the remainder on antibodies, their properties and uses. The editorial points out that immunology covers a wider area than this—that its boundaries, in fact, are indefinite and anticipates papers both on the wider aspects, and on the limited one of freedom from injury, where much interesting work is being done at present.

Notes on contributors

V. V. BELOUSSOV,

Was born in 1907. He is a Correspondent Member of the Academy of Sciences of the U.S.S.R. and is Chairman of the Soviet Academy Committee on Geodesy and Geophysics. He has worked mainly in the field of tectonics, studying in particular the history of the wave movements of the earth's core and the geological development of the Caucasus range. The main results of his work are embodied in Общая Тектоника (General Tectonics), Moscow 1948. He is also the author of Очерки Геохимии природных Газов (Essays on the Geochemistry of Natural Gases), Leningrad, 1937, and Большой Кавказ (The Great Caucasus), Leningrad, 1938–40, besides other works.

ANTOINETTE PIRIE,
M.A., Ph.D.,

Was born in London in 1905 and educated at Newnham College, Cambridge. She worked in the Biochemical Laboratory, University of Cambridge, under Professor Sir F. G. Hopkins until 1940, when she moved to London and then Oxford to work on the biochemistry of the eye. She is now Reader in Ophthalmology, University of Oxford. Her research interests include the biochemical changes that initiate cataract and the relation of the biochemistry of the eye to the functions of its separate parts. Together with Dr Ruth van Heyningen she has written 'The Biochemistry of the Eye'.

M. F. PERUTZ,
Ph.D., F.R.S.,

Was educated at the Universities of Vienna and Cambridge and is Director of the Medical Research Council's Molecular Biology Unit at the Cavendish Laboratory, Cambridge. He is also a Reader at the Davy Faraday Research Laboratory at the Royal Institution in London. His main field is X-ray crystallography, particularly research into the structure of haemoglobin and the elucidation of the physical and chemical properties of protein crystals. A love of mountaineering and ski-ing brought him into contact with glacier research, to which he has made several contributions.

WŁODZIMIERZ HUBICKI,
M.A., Ph.D.,

Was born in Borysław in 1914 and educated at the University of Cracow. In 1938 he became a research assistant in inorganic chemistry at this University and during the war was a teacher in the Technical School at Cracow. Since 1947 he has been professor of inorganic chemistry at the Marie Curie-Skłodowska University at Lublin. From 1949 until 1952 he was the Dean and since 1956 the Vice-Rector. He is also Professor at the Institute for the History of Science of the Polish Academy of Science and the head of the section for history of chemistry. He is the author of many research papers on inorganic and analytical chemistry and on the early history of chemistry.

H. P. BROIDA,
A.B., A.M., Ph.D.,

Was born in Aurora, Colorado, in 1920 and studied at the Universities of Colorado and Harvard. In 1949, after teaching at Wesleyan and at Harvard, he joined the National Bureau of Standards where he has done research on the spectroscopy of flames, chemical kinetics, diatomic spectra, isotope analysis, medical instrumentation, and more recently, as an outgrowth of his work in flames, on free radical production and stabilization. In 1952–53 he spent a year at Imperial College, London, as a Guggenheim Fellow and in 1956 he received the Arthur S. Flemming award of the Washington Junior Chamber of Commerce.

E. G. C. BURT,
B.Sc., A.M.I.E.E.,

Was born in Somerset in 1922 and educated at Yeovil School and London University (Queen Mary College). He graduated in electrical engineering in 1943; served as an R.A.F. officer from 1943 to 1947, some of this time being spent at the Royal Aircraft Establishment in the Radio Department and Instruments Department. Joined the Guided Weapons Department in 1947 as Scientific Officer. In 1955 he became Senior Principal Scientific Officer and Head of the Dynamic Analysis Division, which is concerned with the theoretical aspects of the guidance and control of missiles and satellites. He has published papers on analogue computing techniques, on the theory of servo mechanisms, and on the effects of random disturbances in such systems.

Some books received

(*Note.* Mention of a book on this page does not preclude subsequent review.)

ARCHAEOLOGY

Sibrium, *Vol. III, compiled by Mario Bertolone. Pp. xiv* + 268. *Centro di Studi Preistorici ed Archeologici, Varese.* 1958.

BIOCHEMISTRY

The Chemical Dynamics of Bone Mineral, *by W. F. Neuman and M. W. Neuman. Pp. xi* + 209. *The University of Chicago Press, Chicago; Cambridge University Press, London.* 1958. 37*s.* 6*d. net.*

Methods of Biochemical Analysis, *Vol. VI, edited by D. Glick. Pp. ix* + 358. *Interscience Publishers Inc., New York; Interscience Publishers Ltd., London.* 1958. $8.50 *net.*

Organic Peroxides in Radiobiology, *edited by M. Haïssinsky. Pp. vi* + 153. *Pergamon Press Ltd., London.* 1958. 60*s. net.*

BIOLOGY

Causes de la répartition des êtres vivants, *by Raymond Furon. Pp.* 164. *Masson et Cie, Paris.* 1958. *Fcs.* 1000 *net.*

Die Welt der vernachlässigten Dimensionen in der Biologie, *by A. Frey-Wyssling. Pp.* 18. *Polygraphischer Verlag A.G., Zürich.* 1958. *Sw. Fcs.* 3.10 *net.*

The Dynamics of Bacterial Populations Maintained in the Chemostat, *by H. Moser. Pp. iv* + 136. *Carnegie Institution of Washington Publication* 614, *Washington, D.C.* 1958. *Paper covers,* $1.15 *net; cloth covers,* $1.40 *net.*

Embryos and Ancestors (*third edition*), *by Sir Gavin de Beer. Pp. xii* + 197. *Oxford University Press, London.* 1958. 25*s. net.*

A Handbook on Evolution. *Pp. x* + 110. *British Museum (Natural History), London.* 1958. 5*s. net.*

Looking at Chromosomes, *by J. McLeish and B. Snoad. Pp. vii* + 87. *Macmillan & Co. Ltd., London; St. Martin's Press, New York.* 1958. 16*s. net.*

L'origine photochimique de la vie, *by A. Dauvillier. Pp.* 214. *Masson et Cie, Paris.* 1958. *Fcs.* 1300 *net.*

BOTANY

Ergebnisse der Österreichischen Waldstandsaufnahme 1952/56. *Vol. VI,* Steiermark. *Pp.* 147. *Forstliche Bundes-Versuchsanstalt Mariabrunn, Vienna.* 1958.

CHEMISTRY

Chemical Thermodynamics, *by F. T. Wall. Pp. vii* + 422. *W. H. Freeman & Co. Inc., San Francisco; Bailey Bros. and Swinfen Ltd., London.* 1958. 68*s. net.*

Chimie minérale, *Vol. II, by L. Hackspill, J. Besson, and A. Herold. Pp.* 867–1681. *Presses Universitaires de France, Paris.* 1958. *Fcs.* 3600 *net*

Current Trends in Heterocyclic Chemistry. (Proceedings of a Symposium held at the Australian National University, Canberra, 2–4th September, 1957 under the auspices of The Chemical Society), *edited by A. Albert, G. M. Badger, and C. W. Shoppee. Pp. ix* + 170. *Butterworth's Scientific Publications Ltd., London.* 1958. 30*s. net.*

Encyclopedia of Chemical Reactions, *Vol. VII, compiled by C. A. Jacobson and edited by C. A. Hampel. Pp.* 479. *Reinhold Publishing Corporation, New York; Chapman and Hall Ltd., London.* 1958. 102*s. net.*

New Chemistry. *Pp. xi* + 206. *G. Bell & Sons Ltd., London.* 1958. 13*s.* 6*d. net.*

The Pentaerythritols, *by E. Berlow, R. H. Barth, and J. E. Snow. Pp. vii* + 317. *Reinhold Publishing Corporation, New York; Chapman and Hall Ltd., London.* 1958. 80*s. net.*

Physical and Azeotropic Data, *by G. Claxton. Pp. v* + 146. *The National Benzole and Allied Products Association, London.* 1958.

Bentley and Driver's Qualitative Chemical Analysis (*fifth edition*), *revised by J. E. Driver. Pp.* 47. *Hong Kong University Press, Hong Kong; Oxford University Press, London.* 1958. 7*s.* 6*d. net.*

Quantitative Analysis (*fourth edition*), *by W. C. Pierce, E. L. Haenisch, and D. T. Sawyer. Pp. xiii* + 497. *John Wiley & Sons Inc., New York; Chapman and Hall Ltd., London.* 1958. 46*s. net.*

The Teaching of Chemistry (*second edition*), *by N. F. Newbury. Pp. xv* + 294. *William Heinemann Ltd., London.* 1958. 21*s. net.*

ENGINEERING

The Calculations of Deformations of Welded Metal Structures, *by N. O. Okerblom. A Translation from the Russian. Pp. viii* + 234. *Her Majesty's Stationery Office, London.* 1958. 15*s. net.*

A Guide to Nuclear Energy, *by R. F. K. Belchem. Pp. vii* + 77. *Sir Isaac Pitman & Sons Ltd., London.* 1958. 10*s. net.*

GEOPHYSICS

Veröffentlichungen des Instituts für Meeresforschung in Bremerhaven, *Vol. V, Pt. II, edited by H. Freidrich. Pp.* 135–209. *Kommissionsverlag Franz Leuwer,* Bremen. 1958.

Le volcanisme lunaire et terrestre, *by A. Dauvillier. Pp.* 300. *Editions Albin Michel. Paris,* 1958. *Fcs.* 1200 *net.*

LINGUISTICS

Science Students' Guide to the German Language, *by A. F. Cunningham. Pp. xiii* + 186. *Oxford University Press, London.* 1958. 12*s.* 6*d. net.*

MEDICINE

Diététique thérapeutique, *by J. Trémolières, A. Mossé and L. Delbès. Pp.* 555. *G. Doin et Cie, Paris.* 1958. *Fcs.* 6500 *net.*

Operable Herzleiden. Einführung in Klinik, Diagnostik und Operationsmöglichkeiten, *by J. Jacobi and M. Loeweneck. Pp. viii* + 175. *Georg Thieme Verlag, Stuttgart.* 1958. *DM* 49.50 *net.*

PHYSICS

Concepts of Classical Optics, *by J. Strong. Pp. xxi* + 692. *W. H. Freeman & Co. Inc., San Francisco; Bailey Bros. and Swinfen Ltd., London.* 1958. 80*s. net.*

Heat, *by A. J. Woodall. Pp. xii* + 373. *The English Universities Press Ltd., London.* 1958. 21*s. net.*

Optique électronique, *Vol. II,* Microscopes, diffractographes, spectrographes de masse, oscillographes cathodiques, *by P. Grivet. Pp.* 339. *Bordas, Paris.* 1958.

Proceedings of the Symposium on the Role of Solid State Phenomena in Electric Circuits, New York, April 23, 24 and 25, 1957. *Vol. VII. Pp. xvi* + 339. *Polytechnic Institute of Brooklyn, Brooklyn; distributed by Interscience Publishers Inc., New York; Interscience Publishers Ltd., London.* 1958. $5.00 *net.*

TECHNOLOGY

Recent Advances in Gelatin and Glue Research, *edited by G. Stainsby. Pp.* 277. *Pergamon Press Ltd., London.* 1958. 70*s. net.*

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